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# The microcline-sanidine stability relations

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(*Received* 3 *October* 1953)

ABSTRACT

States that are structurally intermediate between the triclinic and monoclinic modifications of $KAlSi_3O_8$ are described and discussed with relation to order-disorder in alloys. X-ray powder diffraction data on microcline are given. Intermediate states were produced by heating microcline well above the temperature of its inversion to sanidine. These states could not be produced in the approximate range of the transition, either by dry heating, or hydrothermally. Microcline is readily converted to sanidine, however, under hydrothermal conditions at temperatures well below those necessary in the dry state. The lowest temperature observed for the hydrothermal conversion of a microcline to sanidine was 525°C. The hydrothermal conversion takes place by a mechanism that differs from that of the simple diffusive transformation that occurs when microcline is heated dry above *ca.* 1000°C. The mechanism of this conversion, which involves solution of microcline and re-precipitation of sanidine is discussed. Some doubt is cast on the validity of using this type of conversion in placing transformation temperatures in the alkali feldspar system.

## INTRODUCTION

The polymorphic relations of triclinic and monoclinic potash feldspars have long been clouded. Evidence relating to this subject has slowly accumulated throughout the years, and is summarized by LAVES (1950, 1952). It is now known that microcline (triclinic) and sanidine (monoclinic) represent two distinct polymorphs of $KAlSi_3O_8$. "Orthoclase" is not considered to be a stable polymorph (see above reference). It has also become quite apparent that microcline is stable at low temperatures, and sanidine at high temperatures, but the temperature of transformation has only been guessed at or estimated by indirect methods. Sanidine is the only K-feldspar that has been synthesized with certainty. An experimental determination of the microcline-sanidine conversion will be presented, but it is convenient to first discuss some relations pertinent to the problem.

## THEORETICAL CONSIDERATIONS

The microcline-sanidine relations are best explained by the assumption that the Al-Si distribution is disordered in sanidine, and ordered in microcline (see summary of evidence by LAVES, 1952). The fact that the present authors, as well as previous workers, have been unable to synthesize microcline directly or to convert sanidine to microcline, makes it necessary to discuss the equilibrium relations by analogy with known experimental systems, considering only structural geometry, and disregarding bonding forces. A large amount of work has been done on order-disorder relations in alloys. Figs. 1 and 2 represent the state-temperature diagrams of two well-known alloys, $Cu_3Au$, and CuZn. In these diagrams the degree of order is given as a function of temperature and each "degree of order" is represented by an intermediate state stable at some particular temperature. In Figs. 1 and 2, $T_0$ is considered as the temperature where observable disorder sets in, and $T_c$ as the critical temperature above which no long range order is observed.

The intermediate states can be produced either under equilibrium or non-equilibrium conditions. Under equilibrium conditions the intermediate states can appear only in the range of temperature between $T_0$ and $T_c$. For example, in Fig. 2, the state $S(i)$ is stable only at the temperature $T(i)$. It is important to note, however, that any intermediate state may be *metastably* produced at temperatures other than those in the range $T_0$ to $T_c$. Disordered material may become

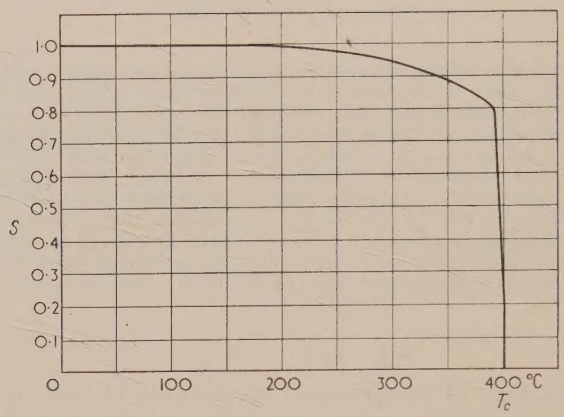


Fig. 1. State-temperature diagram for $Cu_3Au$. After KEATING and WARREN (1951). $S$ = long range order coefficient.

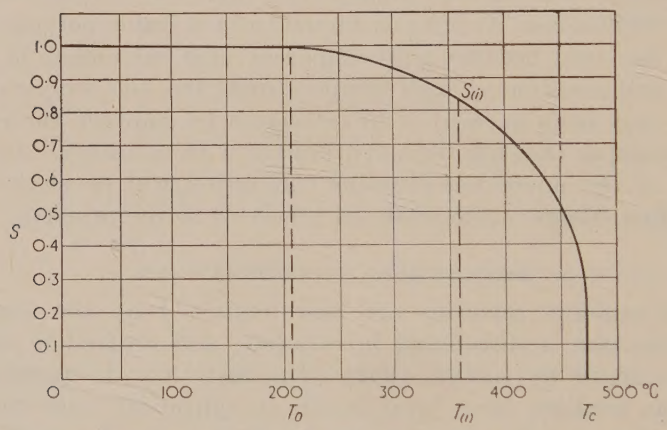


Fig. 2. State-temperature diagram for CuZn ($\beta$-brass). After CHIPMAN and WARREN (1950). $S$ = long range order coefficient; $T_0$, $T_{(i)}$ and $S_{(i)}$ added by the writers for the present discussion.

partially ordered at temperatures below $T_0$, and ordered material may become partially disordered at temperatures above $T_c$.

These considerations, applied to the microcline-sanidine transition would lead one to expect that intermediate states might exist. In alloy systems the presence of complete order or of intermediate states of order is usually determinable by observation of superstructure reflections in X-ray photographs. The intensity distribution of these reflections is a measure of the degree of order,

and they are absent in the completely disordered material.[1] In the case of the potash feldspars, the structures are such that ordering of Al and Si atoms does not develop a superstructure. It is fortunate, however, that the disordered material (sanidine) is monoclinic, whereas the ordered material (microcline) is triclinic. The triclinic nature of microcline can be expressed by the deviation of the lattice angles $\alpha$ and $\gamma$ (or $\alpha^*$ and $\gamma^*$ in reciprocal space) from 90°.[2] Intermediate states should show smaller deviations. The amount of this deviation can be called the "triclinicity." The triclinicity can therefore be used as a function of the degree of order and might be expected to show all variations between the extremes of sanidine and microcline. These variations have been observed by the writers in natural feldspars, and produced in heat-treated samples.

## Determination of Triclinicity

The x-ray diffraction diagrams of microcline and monoclinic K-feldspar are readily distinguishable (Laves, 1950). In Fig. 3 (a) and (f) are reproduced powder photographs of a microcline and a sanidine. A number of reflections from the monoclinic structure are split into doublets with significant separation in the pattern of the triclinic material. MacKenzie (1952) noted this separation of certain peaks on x-ray spectrometer patterns, and suggested that two peaks that he thought were probably (130) and ($1\bar{3}0$) be used for noting the triclinic character of microcline. MacKenzie's identification of these peaks is correct as can be seen in Table 1, which contains x-ray powder data for microcline and sanidine. Among the doublets convenient for distinguishing monoclinic from triclinic K-feldspar, the pair (131) and ($1\bar{3}1$) appeared to be most useful for the present work.

The difference in spacing of the (131) and ($1\bar{3}1$) lines can be used as a measure of triclinicity. Intermediate states are readily observed through the use of these reflections. The (131) line is clearly resolved, and the influence of ($22\bar{2}$) on the ($1\bar{3}1$) reflections not deleterious. Reference to Table 1 and footnote 3 of this table indicates that the ($1\bar{3}1$) reflection has an intensity of approximately 6 times that of ($22\bar{2}$).

Obviously, the triclinicity decreases with increasing disorder in the potash feldspars. Therefore, with increasing disorder, the spacings of ($hkl$) and ($h\bar{k}l$) approach each other, and the difference becomes zero in the monoclinic case. Table 1 also shows spacings and indices of a monoclinic sanidine.

Fig. 4 is a diagrammatic representation of the disorder-temperature relations in the potash feldspars. The value of $d(131)$–$d(1\bar{3}1)$ is taken as a measure of the triclinicity and of the degree of disorder.

The largest value of $d(131)$–$d(1\bar{3}1)$ observed by the writers is slightly under 0·08 (microcline from the Orijärvi area, Finland). The values $d(131)$–$d(1\bar{3}1)$ can, for the sake of convenience, be converted to a scale from zero to unity. If this scale is set so that the most triclinic microcline observed has a value very close to unity, and if the above microcline with the value $d(131)$–$d(1\bar{3}1) = 0{\cdot}08$ is used

[1] Only long-range order is considered in this discussion.

[2] The average values of the triclinic angles of several microclines measured by Laves (1950) are $\alpha = 90° 39'$, $\gamma = 87° 47'$, $\alpha^* = 90° 22'$, $\gamma^* = 92° 10'$.

*Table 1. X-ray powder diffraction data on microcline and sanidine*

| Microcline | | | | | | Sanidine[1] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| *hkl* | $\frac{1}{d^2}$ | $2\theta$ Calculated ($FeK_\alpha$) | $2\theta$ Observed[2] | Intensity Observed | Intensity, from Single Crystal[3] | *hkl* | $\frac{1}{d^2}$ | $2\theta$ Calculated ($FeK)_\alpha$ | Intensity Observed[1] | Intensity, from Single Crystal[3] |
| 110 | 02200 | 16·5 | | | 15 | 110 | 02259 | 16·8 | 1 | 13 |
| $1\bar{1}0$ | 02358 | 17·1 | } 17·25 | 2 | 13 | 020 | 02356 | 17·1 | } 1 | 16 |
| 001 | 02370 | 17·1 | | | 13 | 001 | 02407 | 17·2 | } | 15 |
| 020 | 02383 | 17·2 | | | 15 | $11\bar{1}$ | 02903 | 19·0 | 2 | 15 |
| $11\bar{1}$ | 02840 | 18·8 | 18·85 | 1 | 13 | 021 | 04763 | 24·4 | | 9 |
| $\bar{1}11$ | 02964 | 19·2 | | | 10 | $20\bar{1}$ | 05560 | 26·4 | 8 | 21 |
| 021 | 04718 | 24·3 | 24·2 | 1 | 16 | 111 | 06428 | 28·4 | 3 | 16·5 |
| $02\bar{1}$ | 04787 | 24·5 | | | 3 | 200 | 06678 | 29·0 | 1 | 15 |
| $20\bar{1}$ | 05610 | 26·5 | 26·6 | 6 | 21 | 130 | 06971 | 29·6 | 10 | 21 |
| 111 | 06300 | 28·1 | 28·2 | 3 | 20 | $13\bar{1}$ | 07615 | 31·0 | 4 | 17 |
| $1\bar{1}1$ | 06493 | 28·6 | 28·6 | 1— | 18 | $22\bar{1}$ | 07916 | 31·6 | 3 | 15 |
| 200 | 06734 | 29·1 | | | 18 | $11\bar{2}$ | 08362 | 32·5 | 8 | 18·5 |
| 130 | 06807 | 29·3 | 29·3 | 5 | 23 | 220 | 09034 | 33·7 | 9 | 19 |
| $1\bar{3}0$ | 07282 | 30·3 | 30·3 | 4 | 23 | $20\bar{2}$ | 09256 | 34·3 | 9 | 21 |
| $13\bar{1}$ | 07482 | 30·7 | 30·85 | 1— | 20 | 040 | 09424 | 34·6 | 6 | 20 |
| $22\bar{1}$ | 07710 | 31·2 | | | 16 | 002 | 09628 | 35·0 | 10 | 22 |
| $\bar{1}31$ | 07853 | 31·5 | 31·45 | 2 | 17 | 131 | 11140 | 37·7 | 8 | 19·5 |
| $11\bar{2}$ | 08220 | 32·2 | } 32·35 | 5 | 22 | $22\bar{2}$ | 11612 | 38·5 | 1 | 14·5 |
| $\bar{2}21$ | 08275 | 32·4 | | | 11 | 041 | 11831 | 38·9 | 2 | 19·5 |
| $\bar{1}12$ | 08309 | 32·4 | | | 21 | 022 | 11984 | 39·2 | 1 | 15 |
| 220 | 08800 | 33·4 | 33·45 | 5 | 21 | 201 | 12610 | 40·2 | | 6 |
| $20\bar{2}$ | 09225 | 34·2 | 34·25 | 4 | 21·5 | $31\bar{1}$ | 12734 | 40·4 | | 7 |
| $2\bar{2}0$ | 09434 | 34·6 | } 34·75 | 10 | 21 | $13\bar{2}$ | 13074 | 41·0 | 4 | 17·5 |
| 002 | 09479 | 34·7 | | | 21 | $31\bar{2}$ | 14668 | 43·6 | 4 | 17·5 |
| 040 | 09531 | 34·8 | | | 23 | 221 | 14966 | 44·0 | | 13 |
| 131 | 10872 | 37·3 | 37·35 | 4 | 22 | $24\bar{1}$ | 14984 | 44·0 | 6 | 18 |
| $22\bar{2}$ | 11387 | 38·2 | } 38·15 | 5 | 17 | 112 | 15411 | 44·7 | | 15 |
| $1\bar{3}1$ | 11451 | 38·3 | | | 22 | 310 | 15615 | 45·0 | | 16 |
| 022 | 11793 | 38·9 | | | 19 | 240 | 16102 | 45·8 | | 14 |
| 041 | 11832 | 38·9 | | | 21 | 150 | 16395 | 46·2 | | — |
| $\bar{2}22$ | 11856 | 39·0 | 39·0 | 5 | 14 | $15\bar{1}$ | 17039 | 47·1 | | 17 |
| $02\bar{2}$ | 11931 | 39·1 | | | 17·5 | $33\bar{1}$ | 17446 | 47·7 | Reflec- | 16 |
| $04\bar{1}$ | 11970 | 39·2 | | | 21 | $20\bar{3}$ | 17767 | 48·2 | tions | — |
| 201 | 12598 | 40·2 | | | 7 | $11\bar{3}$ | 18634 | 49·4 | not | 14·5 |
| $31\bar{1}$ | 12656 | 40·3 | | | 1 | $24\bar{2}$ | 18680 | 49·5 | sharp[4] | — |
| $13\bar{2}$ | 12896 | 40·7 | 40·9 | 1 | 17·5 | 042 | 19052 | 50·0 | | — |
| $\bar{3}11$ | 13096 | 41·0 | } 41·1 | 2 | 13 | $33\bar{2}$ | 19380 | 50·5 | | 13 |
| $\bar{1}32$ | 13164 | 41·2 | | | 18·5 | $22\bar{3}$ | 20123 | 51·5 | | 9 |
| $31\bar{2}$ | 14541 | 43·4 | } 43·4 | 3 | 13 or 20 | 132 | 20123 | 51·5 | | 6·5 |
| $24\bar{1}$ | 14577 | 43·4 | | | 17 | 330 | 20327 | 51·8 | | 11 |
| $22\bar{1}$ | 14635 | 43·5 | | | 12 | 151 | 20564 | 52·1 | | 15 |
| $\bar{3}12$ | 14947 | 44·0 | | | 13 or 20 | 060 | 21204 | 53·0 | 1 | 19 |
| $11\bar{2}$ | 15139 | 44·3 | 44·25 | 2 | 21 | | | | | |
| $2\bar{2}1$ | 15332 | 44·6 | | | 16 | | | | | |
| $1\bar{1}2$ | 15366 | 44·6 | | | 17 | | | | | |
| 310 | 15510 | 44·9 | } 45·0 | 3 | 18 | | | | | |
| 240 | 15632 | 45·0 | | | 14 | | | | | |
| $\bar{2}41$ | 15705 | 45·1 | | | 21 | | | | | |
| $3\bar{1}0$ | 15985 | 45·6 | 45·65 | 1— | 19? | | | | | |
| 150 | 16180 | 45·9 | | | 0? | | | | | |
| $2\bar{4}0$ | 16899 | 46·9 | } 47·0 | 1 | 15 | | | | | |
| $1\bar{5}0$ | 16972 | 47·0 | | | 12 | | | | | |
| $15\bar{1}$ | 16976 | 47.0 | | | 20 | | | | | |
| $33\bar{1}$ | 16981 | 47·1 | | | 19 | | | | | |
| $\bar{1}51$ | 17422 | 47·7 | } 47·8 | 1— | 17 | | | | | |
| $20\bar{3}$ | 17580 | 47·9 | | | ? | | | | | |
| $24\bar{2}$ | 18261 | 48·9 | | | 12 | | | | | |
| $\bar{3}31$ | 18303 | 49·0 | } 49·05 | | 17 | | | | | |
| $11\bar{3}$ | 18339 | 49·0 | | | 16? | | | | | |
| $\bar{1}13$ | 18394 | 49·1 | | | 16? | | | | | |
| 042 | 18872 | 49·8 | | | 12 | | | | | |
| $33\bar{2}$ | 18901 | 49·8 | | | 13 | | | | | |
| $04\bar{2}$ | 19149 | 50·2 | | | 10 | | | | | |
| $\bar{2}42$ | 19252 | 50·3 | | | — | | | | | |
| 132 | 19677 | 50·9 | | | ? | | | | | |
| $22\bar{3}$ | 19750 | 51·0 | | | 11 | | | | | |
| 330 | 19800 | 51·1 | | | 10 | | | | | |
| $\bar{3}32$ | 20119 | 51·5 | } 51·55 | 0·5 | 13 | | | | | |
| 151 | 20124 | 51·5 | | | 14 | | | | | |
| $\bar{2}23$ | 20176 | 51·6 | | | 9 | | | | | |
| $1\bar{3}2$ | 20359 | 51·8 | | | 9·5 | | | | | |
| $31\bar{3}$ | 21167 | 52·9 | | | 7 | | | | | |
| $3\bar{3}0$ | 21226 | 53·0 | | | 13 | | | | | |
| $1\bar{5}1$ | 21262 | 53·1 | | | 14 | | | | | |
| 241 | 21426 | 53·3 | } 53·25 | 5 | 20 | | | | | |
| 060 | 21445 | 53·3 | | | 24 | | | | | |

Calculation of reflections carried out only to (060), at $2\theta = 53.3$ for $FeK_\alpha$ radiation. All possible reflections in this range are given.

[1] Sanidine lattice constants, spacings, and powder intensities from DONNAY and DONNAY (1952), on soda-free synthetic $KAlSi_3O_8$. Recalculated for $FeK_\alpha$ radiation, and with certain additions.

[2] Microcline from Madagascar, albite lines omitted.

[3] Estimated intensities from single-crystal rotation photographs. Here, 1 unit = a factor of $\sqrt{2}$ in intensity (i.e., 1–24 = actual intensity range of approximately 1–4000. See LAVES, 1950, p. 561).

[4] Intensities not given by DONNAY and DONNAY.

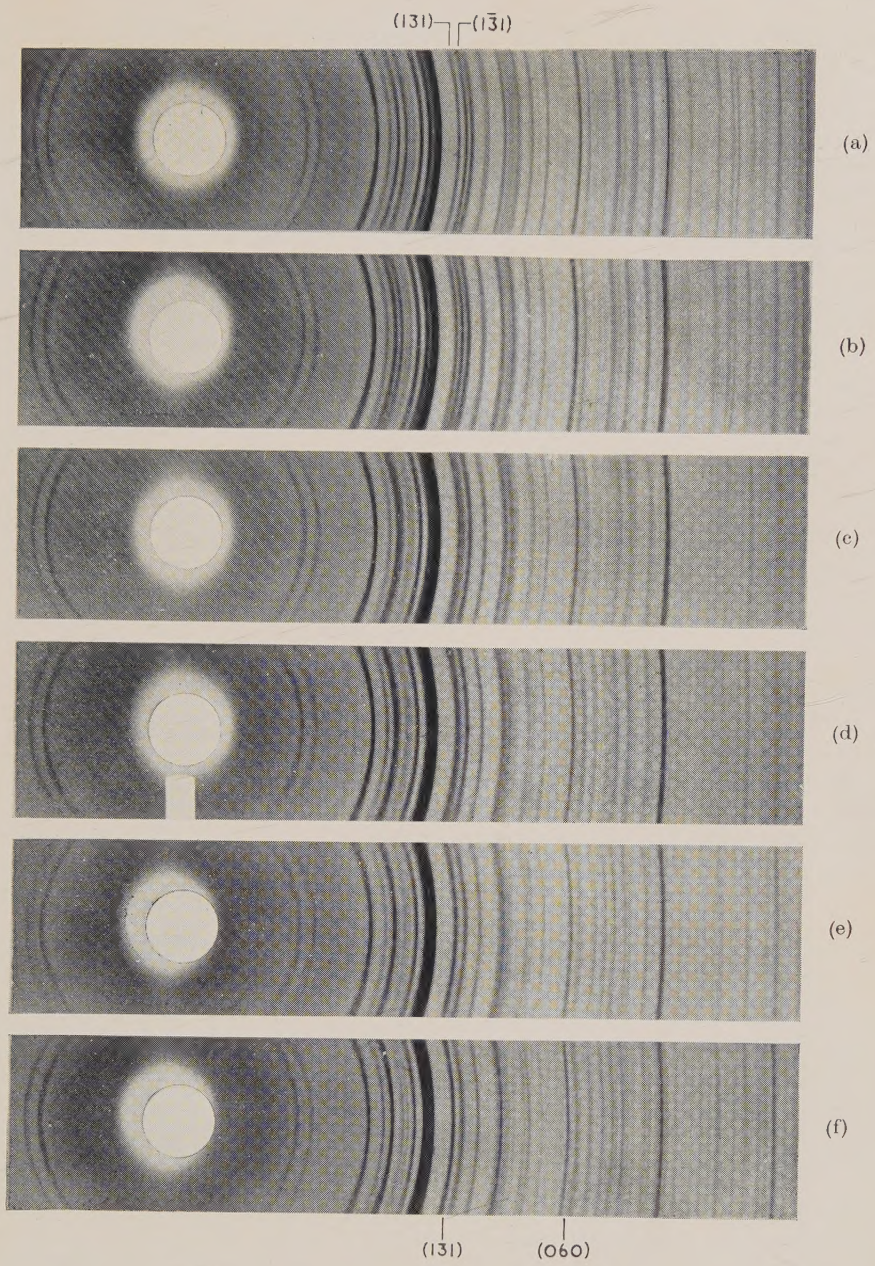


Fig. 3. X-ray powder diffraction photographs of $KAlSi_3O_8$ samples. $FeK_\alpha$ radiation.

(a) Microcline (Pontiskalk, Switzerland), $\Delta = 0{\cdot}96$.
(b) Microcline (Pontiskalk, Switzerland), heated 144 hours at 1050°, $\Delta = 0{\cdot}77$.
(c) Microcline (Pontiskalk, Switzerland), heated 240 hours at 1050°, $\Delta = 0{\cdot}53$.
(d) Microcline (Pontiskalk, Switzerland), heated 336 hours at 1050°, $\Delta \sim 0{\cdot}2$–$0{\cdot}3$.
(e) Microcline (Pontiskalk, Switzerland), sanidinized by heating 720 hours at 1050°C, $\Delta$ near or $= 0$.
(f) Sanidine (synthetic $KlSi_3O_8$).

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as a standard, a conversion factor, $k$, is set by the expression $0{\cdot}08 \times k = 1$. Therefore $k = 12{\cdot}5$. A measure of triclinicity, $\Delta$, can now be defined:

$$\Delta = 12{\cdot}5[d(131)-d(1\bar{3}1)]$$

By this definition, a potash feldspar with $\Delta = 1$ would be considered fully ordered. If $\Delta = 0$, the feldspar is disordered, at least to the extent that its lattice has monoclinic symmetry.[1]

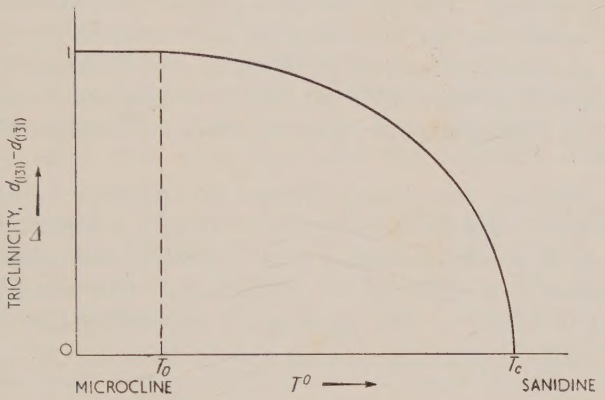



Fig. 4. Diagrammatic representation of the disorder-temperature relations in potash feldspars.

## Effect of Dry Heat Treatment on Microcline

The effect of long heat treatments at high temperature on the optics of microcline has been experimentally studied by Dittler and Köhler (1925) and by Spencer (1937). Spencer observed, in addition to the change in refractive indices and specific gravity in short heatings (undoubtedly induced by the solution of some albite) the following:

"In comparison with the corresponding orthoclases, the six microclines show a characteristic resistance to change on prolonged heating. Thus specimens *E* and *H* of the orthoclase-microperthite series, with approximately the same soda-feldspar content as the microclines, show axial angles 2V 29° and 22° in the symmetry-plane after 200 hours at 1075°C. The optic angles of the microclines, by the same treatment, drop from 2V 70–80° to 30–50°, the optic axial plane remaining normal to (010). Microclines *U* and *V* showed unexpected changes after heating for 300 hours at 1075°C; the optic axial angles were reversed into the symmetry plane to 2V 44° and 16°, respectively. At the same time the fine microcline twinning visible on (001) was destroyed. It is seen that these glassy or semi-glassy microclines are more easily sanidinized than adularia of corresponding composition.

"Previous attempts to convert microcline to the homogeneous monoclinic orthoclase form by heat-treatment have yielded conflicting results. Mäkinen and previous investigators found that the cross-hatch structure was not destroyed on heating to near the melting-point of the feldspar.

"Dittler and Köhler by heating microcline-microperthite for 500–700 hours at 1000°C found that the cross-hatching disappeared, leaving a mineral with the characteristics of orthoclase. More recently, Barth heated low-soda microcline for 300–600 hours at 1000°C, after which the mineral was still triclinic.

[1] Using 114·53 mm diameter powder cameras and $FeK_\alpha$ radiation, an accuracy of $\Delta$ exceeding $\pm 0{\cdot}05$ does not appear justified.

"These variable results probably represent the difference in behaviour of different microcline specimens. The writers' results show that the semi-glassy, finely twinned microclines are much less resistant to heat-treatment than the coarsely twinned varieties with 'vein' perthite, especially when the optic axial angle is initially large. There is little doubt that prolonged heating at 1075°C would convert even the latter into the homogeneous form. The character of the transformation seems to be more abrupt than that found in the orthoclase-microperthite series, and resembles the changes undergone by albite."

SPENCER as well as DITTLER and KÖHLER noted intermediate values of 2V in heat-treated microclines. The optical data suggest intermediate structures.

BARTH (1931) questioned the relevance of such work to the problem of polymorphism. With particular reference to DITTLER and KÖHLER'S work, he stated that inasmuch as perthites were involved, the heat-treatment can with certainty only be considered as homogenization and therefore not necessarily a polymorphic change.

To avoid this criticism, the present writers investigated a single-phase microcline from Switzerland, virtually soda free.[1] In Fig. 3 is shown a series of x-ray powder photographs of the heat-treated (1050°C) Swiss microcline. An untreated sample and a sanidine are included for comparison. The data as a function of time are presented in Table 2. The decrease in triclinicity through intermediate

*Table 2. Change in triclinicity produced in Swiss microcline* by dry heating*

| *Temperature C* | *Time, Hours* | *Original Δ-value* | *Δ-value of Heated Sample* |
|---|---|---|---|
| 1050° | 48 | 0·96 | 0·92 |
| 1050° | 144 | 0·96 | 0·77 |
| 1050° | 240 | 0·96 | 0·53 |
| 1050° | 336 | 0·96 | 0·29 |
| 1050° | 720 | 0·96 | Monoclinic or virtually so |

* Single-phase, virtually soda-free microcline.

stages and all the way to monoclinic feldspar is clearly shown. Table 3 presents similar data on additional microcline samples (perthitic). It should be kept in

[1] An authigenic microcline from a Swiss limestone (Pontiskalk, Triassic), described by J. P. PERRENOUD (1952). Tiny crystals, <88 microns in size were dissolved out of the limestone. This material is free of albite, and spectrographic analysis by O. JOENSUU shows 0·14% $Na_2O$, 16·5% $K_2O$.

Seven other samples of microcline were used in this study. Brief descriptions follow:

1. Madagascar—Green pegmatitic microcline. Fine to coarse twinning, in places only albite twin law. Some of albite-twin individuals are readily resolved under the low power microscope and show the optics and x-ray pattern of a microcline single-crystal. Contains megascopic, microscopic, and apparently some sub-microscopic albite. Analysis shows 1·9% $Na_2O$, 14·2% $K_2O$, 0·1% CaO, 0·05% $Fe_2O_3$.
2. Finland #1—Microcline varying from white to green, from Tammela, Finland. Finely perthitic. 1·5% $Na_2O$, 14·2% $K_2O$, 0·4% CaO.
3. Finland #2—Pink microcline, Rokonkallio, Sukula, Tammela, Finland. Megascopic perthite.
4. Finland #3—Flesh-coloured, from Heponiitynmäki, Tammela, Finland. Fine megascopic perthite. 2·3% $Na_2O$, 12·0% $K_2O$, 0·1% CaO.
5. Finland #4—White micro-perthite, from a banded granulite rock, Highroad to Sikavuono, Finland. Microcline and monoclinic feldspar of the same composition coexist in this rock. 3·15% $Na_2O$, 11·7% $K_2O$, 1·0% CaO, ~0·3% BaO.
6. Black Hills—White, coarsely perthitic microcline from pegmatite (Custer Mt. Lode), Black Hills, S.D.
7. Michigan—Pink perthitic microcline, from pegmatite near Felch, Michigan.

mind that the temperature of 1050°C used is unquestionably far above the true inversion temperature of microcline to sanidine (see later data) and that the intermediate states developed are metastable at this temperature. Nevertheless, the existence of what appears to be a complete structural series from triclinic microcline to monoclinic sanidine is clearly shown. Natural intermediate potash feldspars are discussed in a following paper.

## The Effect of Soda on Geometry

Microcline usually contains significant amounts of $NaAlSi_3O_8$, either in solid solution, or as perthitic albite, or possibly both. Inasmuch as the effect of soda on the triclinicity of the feldspar would be superimposed on any change produced by degree of order, this effect must be taken into consideration. Experiments, to be described here, show that soda does enter the structure when microclines are heat-treated.

Five different samples of microcline, all containing perthitic albite (perthite lamellae of various size, Finland #4 is a microperthite) were heated at 800°C. This temperature is usually sufficient to homogenize the two phases, coarse "particles" of albite occasionally remaining. Fig. 5 shows x-ray powder diagrams of a typical original and heat-treated (800°C., 6 days) microcline. The strongest line of low-temperature albite, (040) + [(002)?] is indicated by an arrow in the unheated sample of Fig. 5. The fact that homogenization takes place is proved by the disappearance of the albite lines. In accordance with this, shifts in the line spacings of the heated microclines indicate that the volume of the unit cell has become smaller.

The magnitude of $\Delta$ in the original and homogenized samples has not been significantly changed.[1] Thus the 800°C treatment, which produces a microcline with a significant soda content, is not of sufficient severity to disorder the microcline to the extent where our measure of triclinicity is effected.

Table 3 also contains data on the microclines that were homogenized at 800°C. The treatment at 1050°–1070°C, which eventually produces a monoclinic feldspar, must be considered as producing a true polymorphic change, even in samples containing soda.

## Experimental Determination of the Microcline → Sanidine Conversion

The direct determination of the equilibrium relations between microcline and sanidine[2] (i.e., a quantitative determination of the curve schematically represented by Fig. 4) is fraught with difficulties. The kinetics of the microcline $\rightleftarrows$ sanidine transformation involves a diffusive transfer of Al and Si in a network structure.

[1] These results are in conflict with additional experiments, in which soda was diffused into the microcline structure (and potash removed) by sintering a mixture of microcline and a glass of the composition of albite. In these experiments $\Delta$ was changed, in accordance with the idea that microcline and albite form a more or less continuous (pseudostable) solid solution series (see Laves 1952, p. 558). Additional work is necessary to clarify this point on the influence of soda on the microcline geometry, but it is not significant to the thesis of the present paper.

[2] Microcline and sanidine are considered here to be the triclinic and monoclinic forms that have true stability fields. The reasons for this assumption are treated by Laves (1952).

The Al—O and Si—O bonds are exceedingly strong, and must be broken if the transformation in either direction is to take place. A very large activation energy is therefore required for each diffusive exchange. It has been observed that microcline is converted to sanidine by heating dry for relatively long periods of

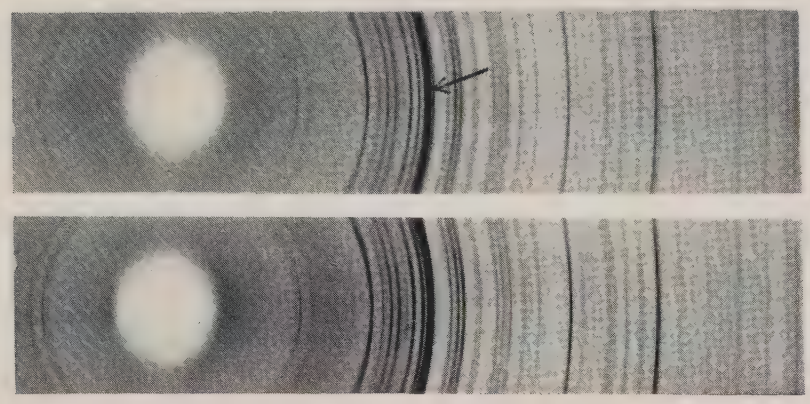
*Table 3. Effect of dry heating on microclines*

| *Microcline, locality* | *T,C°* | *Time, Hours* | *Original Δ-value* | *Δ-value of Heated Sample* | *Remarks* |
|---|---|---|---|---|---|
| Madagascar | 800° | 144 | 0·84 | 0·84 | 1·9% $Na_2O$. Albite dissolved |
| | 1060° | 192 | 0·84 | 0·62 | |
| | 1060° | 336 | 0·84 | 0·62 | |
| | 1060° | 672 | 0·84 | ~0·20 | 131 and $1\bar{3}1$ reflections blended, fuzzy |
| Felch, Michigan | 800° | 168 | 0·92 | 0·95 | Albite dissolved |
| Black Hills, S.D. | 800° | 192 | 0·94 | 0·89 | Albite dissolved |
| Finland #3 | 800° | 192 | 0·96 | 0·92 | 2·3% $Na_2O$. Few larger fragments albite remain |
| | 1065° | 140 | 0·96 | 0·74 | |
| | 1065° | 169 | 0·96 | 0·69 | |
| | 1065° | 284 | 0·96 | 0·61 | |
| | 1065° | 666 | 0·96 | Very low, nearly monoclinic | |
| Finland #4 | 800° | 168 | 0·86 | 0·86 | 3·15% $Na_2O$. Albite dissolved |

time at temperature above *ca.* 1000°C. The reverse, a conversion of sanidine to microcline, has not been observed either by the present or by earlier workers. The preponderance of evidence indicates that, as earlier stated, this dry conversion microcline → sanidine takes place at a temperature well above $T_c$ (critical temperature = transformation temperature) in the time available for experimental work.

## HYDROTHERMAL CONVERSION

Microcline can be converted to sanidine under hydrothermal conditions at temperatures well below those required in the dry state. It is important to note, however, that the use of the word "conversion" in this section refers to a change of the assemblage microcline + $H_2O$ to the assemblage sanidine + $H_2O$. In all of the experiments in which sanidine has been produced from microcline + $H_2O$, the conversion appears to be one of solution of microcline and reprecipitation of sanidine, and not merely a lattice transformation of microcline to sanidine in the one-component system $KAlSi_3O_8$. Finely powdered microcline (crushed such that coarsest grains are approximately 0·02 mm) is converted partially or completely much more rapidly than is coarser material, and will be discussed shortly.



(a)

(b)

Fig. 5. X-ray powder diffraction photographs of original and homogenized microcline (Felch, Michigan).

(a) Original microcline, albite lines present. Arrow points to strongest albite reflection.

(b) Same sample, heated at 800°C for 168 hours. $\Delta$ unchanged, but albite reflections have disappeared.

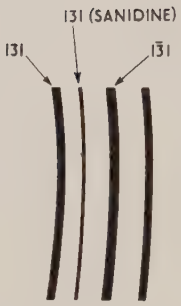



Fig. 6. Schematic drawing of region near (131) in diffraction photographs, representing the development of the (131) sanidine reflection between the (131) and ($1\bar{3}1$) reflections of microcline.

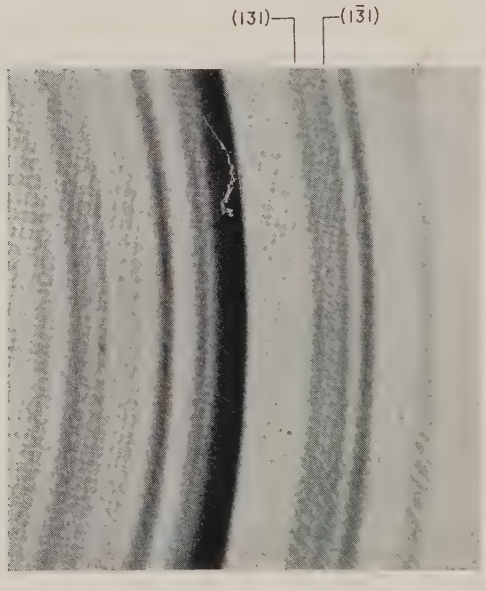



Fig. 7. X-ray powder diffraction photograph (enlarged) of microcline (Madagascar) with (131) reflection of sanidine visible between the (131) and ($1\bar{3}1$) reflections of the microcline.

Tables 4 to 8 list the pertinent hydrothermal data on the conversion of microcline to sanidine.

## Experimental Procedure and General Observations

The finely powdered microcline samples were run hydrothermally in either hydrothermal quenching equipment similar to that described by Tuttle (1948), or in "cold-seal" type bombs also modified after a design by Tuttle (1949). The samples were contained in platinum capsules. The $H_2O$ pressure of all runs listed in Table 4 was 8000 lb/in.$^2$. Pressures as low as 400 lb/in.$^2$ and as high as 30,000 lb/in.$^2$ were used (see Table 6), but little if any effect of these differences on conversion to sanidine was observed. Aside from the effect of pressure on solubility of the microcline one would not expect pressure to significantly affect the conversion under equilibrium conditions, inasmuch as the densities of microcline and sanidine are not greatly different.

An x-ray diffraction photograph was taken of each sample upon completion of a run. Optical examinations did not give reliable information on the finely divided material. None of the hydrothermal experiments produced intermediate states; the development of monoclinic material (sanidine) was the only change produced. The development of sanidine is easily observed; some of the characteristic sanidine lines become visible in the x-ray pattern. Figs. 6 and 7 illustrate this, both schematically and with an actual photograph. The (131) line of the monoclinic material is perhaps most readily observed and was used here. The (130) line of sanidine can be masked by an albite line. The smallest amount of sanidine visible in microcline-sanidine mixtures is a function of particle size, shape, and orientation, and is probably not detectable in quantities of less than 5% under optimum conditions.

Small crystal fragments of several microclines (approximately 0·3 mm) were also treated hydrothermally (individually enclosed in platinum capsules), and used for analysis by single-crystal techniques. The results of these runs could be compared with those on the powdered material, and in addition the surfaces of the fragments could be examined. The "single-crystal"[1] x-ray diffraction photographs showed, in addition to the original microcline reflections, the development of sanidine (monoclinic) reflections. The sanidine reflections usually appeared as very short segments of Debye rings, indicating a slight (maximum 3°) range of orientation with respect to the original microcline. Four days at 800°C (8000 lb/in.$^2$ $H_2O$) produced approximately 25% conversion to sanidine in a microcline from Madagascar. An additional 4 days treatment of the same crystal showed approximately 40% conversion. A crystal of microcline from Norway[2] showed approximately 5–10% conversion in 4 days (800°C, 8000 lb/in.$^2$ $H_2O$). Microscopic observation of these and other similarly treated crystals show the development of oriented monoclinic overgrowths on the parent material. The numerous small overgrowths are responsible for the sanidine reflections in the "single-crystal" photographs, and indicate that conversion takes place at the surface.

[1] The microcline crystals used for this "single-crystal" work were twinned, only after the albite law. It is unfortunate that "single-crystal" and "powder" are the only terms available for the description of x-ray techniques. Twinned crystals fit neither category.

[2] Hunoholmen, Norway. This material described by Laves (1950).

The same conclusion can be drawn from the following experiment. A number of small fragments (of the size used for the single crystal work) of the Madagascar microcline were hydrothermally heated in a single capsule. These fragments were then crushed, and an x-ray powder photograph taken. A treatment of 4 days

*Table 4. Hydrothermal treatment of powdered microclines (8000 lb/in.$^2$ $H_2O$)*

| *Microcline, locality* | *T, °C* | *Time, Hours* | *Results* |
|---|---|---|---|
| Madagascar | 800° | 120 | Completely sanidinized |
| Black Hills | 800° | 47 | Completely sanidinized |
| Madagascar | 750° | 48 | Approx. 90% sanidine, 10% microcline |
| Madagascar | 750° | 192 | Approx. 95% sanidine, 5% microcline |
| Black Hills | 750° | 47 | Approx. 70% sanidine, 30% microcline |
| Michigan | 750° | 50 | Approx. 75% sanidine, 25% microcline |
| Madagascar | 700° | 48 | Approx. 60% sanidine, 40% microcline |
| Madagascar | 700° | 125 | Approx. 50% sanidine, 50% microcline |
| Madagascar | 700° | 500 | Approx. 85% sanidine, 15% microcline |
| Black Hills | 700° | 48 | Approx. 40% sanidine, 60% microcline |
| Switzerland | 700° | 28 | Approx. 20% sanidine, 80% microcline |
| Madagascar | 650° | 144 | Approx. 30% sanidine, 70% microcline |
| Madagascar | 600° | 144 | Approx. 20% sanidine, 80% microcline |
| Madagascar | 600° | 288 | Approx. 25% sanidine, 75% microcline |
| Madagascar | 600° | 672 | Approx. 20% sanidine, 80% microcline |
| Black Hills | 600° | 47 | Approx. 5% sanidine, 95% microcline |
| Michigan | 600° | 48 | Approx. 5% sanidine, 95% microcline |
| Finland #1 | 600° | 24 | Approx. 5–10% sanidine, 95–90% microcline |
| Finland #2 | 600° | 46 | No sanidine visible |
| Finland #3 | 600° | 48 | Trace of sanidine visible |
| Switzerland | 600° | 24 | No sanidine visible |
| Switzerland | 600° | 336 | Possible trace of sanidine? |
| Madagascar | 550° | 24 | Approx. 20% sanidine, 80% microcline |
| Madagascar | 550° | 144 | Approx. 20% sanidine, 80% microcline |
| Madagascar | 550° | 504 | Approx. 20% sanidine, 80% microcline |
| Black Hills | 550° | 48 | Trace of sanidine visible |
| Michigan | 550° | 47 | Trace of sanidine visible |
| Finland #1 | 550° | 24 | Approx. 5–10% sanidine, 95–90% microcline |
| Finland #2 | 550° | 24 | No sanidine visible |
| Finland #3 | 550° | 48 | No sanidine visible |
| Switzerland | 550° | 24 | No sanidine visible |
| Madagascar | 525° | 24 | Approx. 10–20% sanidine, 90–80% microcline |
| Madagascar | 500° | 504 | No sanidine visible |
| Madagascar | 500° | 500 | (Check run) no sanidine visible |
| Switzerland | 500° | 144 | No sanidine visible |

at 800°C showed approximately 30% conversion. The same material, powdered before hydrothermal treatment and therefore having a much greater surface area, shows complete conversion to sanidine in less than half this time.

## Discussion of the Hydrothermal Data

Seven different microcline samples were powdered and treated hydrothermally. These data are summarized in Tables 4–7. Several points are worth noting.

### *Influence of temperature*

Table 4 shows that at 800°C, the conversion is complete in 2 days or less in the two samples run. At 525°C, 10–20% sanidine was developed in 24 hours in the Madagascar microcline. At 500°C, no sanidine was observed in the same material, even after 500 hours. At temperatures intermediate between 525°C and 750°C, various intermediate degrees of conversion were observed in the different microclines. Of the samples used, the Madagascar microcline always showed the greatest

*Table 5. Hydrothermal treatment of Madagascar microcline* 8000 *lb/in.*$^2$ $H_2O$)

| *T, °C* | *Time, Hours* | *Results* |
|---|---|---|
| 800° | 120 | Completely sanidinized |
| 750° | 47 | Approx. 90% sanidine, 10% microcline |
| 750° | 192 | Approx. 95% sanidine, 10% microcline |
| 700° | 48 | Approx. 60% sanidine, 40% microcline |
| 700° | 125 | Approx. 50% sanidine, 50% microcline |
| 700° | 500 | Approx. 85% sanidine, 15% microcline |
| 650° | 144 | Approx. 30% sanidine, 70% microcline |
| 600° | 144 | Approx. 20% sanidine, 80% microcline |
| 600° | 288 | Approx. 25% sanidine, 75% microcline |
| 600° | 672 | Approx. 20% sanidine, 80% microcline |
| 550° | 24 | Approx. 20% sanidine, 80% microcline |
| 550° | 144 | Approx. 20% sanidine, 80% microcline |
| 550° | 504 | Approx. 20% sanidine, 80% microcline |
| 525° | 24 | Approx. 10–20% sanidine, 90–80% microcline |
| 500° | 504 | No sanidine visible |
| 500° | 500 | No sanidine visible (Check run) |

development of sanidine, the Swiss (authigenic) microcline the least. Reference to Tables 2 and 3 indicates, however, that the Swiss microcline is changed *more* rapidly by dry heating at 1050°C than the other specimens treated. A considerable difference in rate of inversion during dry heating of different specimens of microcline and albite was noted by Spencer (1937) and also in the case of albite by Tuttle and Bowen (1950). The mechanism of conversion in the hydrothermal case (microcline + $H_2O \rightarrow$ sanidine + $H_2O$) differs from that in the dry case (microcline $\rightarrow$ sanidine) and will be considered shortly. In Table 5, the results on a single material (microcline from Madagascar) are presented, to better illustrate the influence of temperature.

### *Influence of* $H_2O$ *pressure*

In Table 6 are listed several runs on the Madagascar microcline at pressures widely different from the 8000 lb/in.$^2$ used in all other hydrothermal experiments. No

really significant difference seems to exist in the runs made at 400, 8000, and 30,000 lb/in.$^2$ This justifies the use of a single pressure for the bulk of the experimental work. Some difference is seen in duplicate runs 2 and 3, however, where at 30,000 lb/in.$^2$ in one case a mica appears to develop at the expense of sanidine.

*Table 6. Variation of $H_2O$ pressure with Madagascar microcline*

| *T, °C* | *$H_2O$ pressure, lb/in.$^2$* | *Time, Hours* | *Results* |
|---|---|---|---|
| 550° | 400 | 24 | Approx. 15% sanidine, 85% microcline |
| 550° | 30,000 | 24 | Approx. 5% sanidine, also mica developed |
| 550° | 30,000 | 24 | Approx. 15% sanidine, 85% microcline |
| 500° | 30,000 | 48 | If sanidine present at all, is 5% or less |

It is perhaps worth noting that at 400 lb/in.$^2$, 24 hours at 550°C did not homogenize the perthitic microcline. The albite lines were, however, not observable after 24 hours when a pressure of 30,000 lb/in.$^2$ was used. Further checks on the reproducibility of this effect were not made.

*Influence of time*

Runs of various duration are also listed in Table 4. The influence of time is specifically shown for the Madagascar microcline in Table 5. Although there appears to be, for some samples, continued development of sanidine in runs longer than several days, the effect is certainly not linear. In particular, at lower temperatures (600°C and below), runs of more than a day or two show approximately the same amount of conversion as the shorter runs. Madagascar microcline is converted to approximately 20% sanidine in 144 hours at 600°C, and no further conversion is obvious in 672 hours. The same is true in 24 hours and 504 hours at 550°C. This is additional evidence for the fact that conversion takes place by surface recrystallization. It would appear that a fairly specific amount of recrystallization occurs at a particular temperature, and the particles then become "armoured" against further change. At higher temperatures this effect is less pronounced.

*Influence of soda*

Any soda in solid solution might be expected to affect the microcline-sanidine inversion relations. No data are as yet on hand for the specific influence of soda. Table 7 lists 4 samples that have been analyzed for $Na_2O$, and indicates the degree of conversion noted at 550°C and 600°C (from Table 4). The differences observed in conversion to sanidine cannot be correlated with the soda content of the samples. It must be kept in mind, however, that except for the Swiss microcline, the samples are perthitic. Although some homogenization takes place in the relatively short hydrothermal treatment that produces the conversion, the amount of soda actually present in the microcline of these samples was not determined. In addition, to properly evaluate the influence of soda, the same sample

should be used for all the experiments (i.e., varying soda contents should be produced in a single original sample by various degrees of dry homogenization of a micro or cryptoperthite), so that other contributing influences (see earlier statements) in the inversion characteristics are avoided. Further investigation of this point is necessary.

*Table 7. $Na_2O$ content and conversion behaviour*

| Sample | % | | | | *Amount of Sanidine Formed* | |
|---|---|---|---|---|---|---|
| | $Na_2O$ | $K_2O$ | $CaO$ | $Fe_2O_3$ | 600°C | 550°C |
| Switzerland | 0·14 | 16·5 | 0·5* | N.D. | None | None |
| Finland #1 | 1·5 | 14·2 | 0·4 | N.D. | 5–10% | 5–10% |
| Madagascar | 1·9 | 14·2 | <0·1 | 0·05 | 20% | 20% |
| Finland #3 | 2·3 | 12·0 | 0·1 | N.D. | Trace | None |

Samples analyzed spectrographically by O. Joensuu. Na and K limits of error are ±5% of amount present, Ca ±10% of amount present.

* Undoubtedly high due to carbonate inclusions.

An additional experiment was performed on the Swiss microcline, which is virtually soda-free. Albite (Amelia County, Virginia) was finely pulverized and thoroughly mixed with the Swiss microcline. Approximately 15% albite was used, an amount not uncommon in perthitic microclines. Hydrothermal treatment at 700°C for 24 hours produced an amount of sanidine not significantly different from that in a sample of the unadulterated Swiss material.

*Influence of triclinicity* ($\Delta$)

It was observed in the course of the experimental work that the microcline (Madagascar) most readily converted to sanidine had a $\Delta$-value somewhat lower than most of the other microclines used. Data pertinent to a correlation between triclinicity and ease of conversion to sanidine are collected in Table 8. Experiments 1–7 were carried out with the possibility of this correlation in mind. It is apparent that a dry heat treatment, which produces a decrease in triclinicity, also fosters the subsequent hydrothermal conversion to sanidine. Experiments 8–11 were performed on different portions of a single large crystal; this material shows variations in triclinicity from spot to spot (to be more fully discussed in a following paper on natural potash feldspars). The above tendency is also observed in this material.

The apparent influence of $\Delta$ on ease of conversion is somewhat puzzling. If, as here assumed, a decrease in triclinicity ($\Delta$) is due to a higher degree of disorder, the samples with smaller $\Delta$-values should represent states stable at higher temperatures than those with higher $\Delta$-values; the intermediate material should be

more akin to sanidine than are the more strongly triclinic microclines. If this is the case, one might expect the more disordered microclines to transform less readily than their more ordered counterparts (neglecting differences in activation energies), inasmuch as the free-energy difference between sanidine and the partially ordered material is less than the difference between sanidine and a more ordered material.

*Table 8. Influence of triclinicity on hydrothermal conversion*

| *Microcline, locality* | *Dry Heat-Treatment* | *Original* $\Delta$ | $\Delta$ *after Heat-Treatment* | *Hydrothermal Treatment* (8000 *lb/in.*$^2$ $H_2O$) | *Results* |
|---|---|---|---|---|---|
| 1. Finland #3 | None | 0·96 | — | 600°, 48 hrs | Trace of sanidine visible |
| 2. Finland #3 | 1065°, 140 hrs | 0·96 | 0·66 | 600°, 48 hrs | Approx. 20% sanidine |
| 3. Finland #3 | None | 0·96 | — | 550°, 48 hrs | No sanidine visible |
| 4. Finland #3 | 1065°, 140 hrs | 0·96 | 0·71 | 550°, 48 hrs | Approx. 10% sanidine |
| 5. Switzerland | None | 0·96 | — | 600°, 24 hrs | No sanidine visible |
| 6. Switzerland | None | 0·96 | — | 600°, 336 hrs | Possible trace of sanidine? |
| 7. Switzerland | 1060°, 144 hrs | 0·96 | 0·86 | 600°, 47 hrs | Approx. 5–10% sanidine |
| 8. Finland #1 | None | 0·96 | — | 600°, 24 hrs | Approx. 5–10% sanidine |
| 9. Finland #1 | None | 0·86 | — | 600°, 144 hrs | Approx. 20% sanidine |
| 10. Finland #1 | None | 0·96 | — | 550°, 24 hrs | No sanidine visible |
| 11. Finland #1 | None | 0·81 | — | 550°, 48 hrs | Approx. 25% sanidine |

Another explanation is possible, however. One can assume that a partially ordered material consists of a statistical array of structural regions or fluctuations, differing in degree of disorder, some of which are highly disordered. This material can be considered as having nuclei or "seeds" of sanidine or sanidine-like material, these "sanidine nuclei" being in greater abundance than in a more ordered crystal. This material, under hydrothermal treatment, might tend to develop sanidine as a consequence of internal re-arrangement around the "sanidine nuclei" in addition to the surface recrystallization observed. If this mechanism is functional, it is a further consequence of the entire conversion mechanism, to be discussed shortly. It might also be looked upon as an expression of HEDVALL'S rule (HEDVALL, 1938) which says that any material in the state of transformation has a lower than normal activation energy, and is therefore more reactive.

It must also be kept in mind that the triclinicity may not independently control the observed conversion, but may be consequent upon or accompany other unrecognized or unevaluated factors that are significant. As earlier stated, the relation of triclinicity and soda-content in microcline is not fully evaluated.

## Discussion of the Microcline-Sanidine Inversion Temperature, and the Nature of the Hydrothermal Conversion

If one assumes that the lowest temperature at which microcline shows some conversion to sanidine represents the temperature of the phase transformation (or perhaps a temperature slightly above, due to the sluggishness of the change) several additional assumptions must be made. If the disordering transformation takes place over a significant temperature range (see Fig. 4), then one must assume that inasmuch as intermediate states are not observed during hydrothermal treatment, the upper limit ($T_c$) is the temperature that is experimentally determined. One is also faced with the fact that the lowest temperature at which conversion is observed (in a reasonable time in terms of laboratory experimentation) varies for different microclines. The Madagascar microcline shows some conversion to sanidine at 525°C, the Swiss material and one of the Finnish samples must be taken approximately 100°C higher. One can then assume that the lowest temperature observed is the closest to that of the real inversion, and that the higher temperature required to produce an effect in other samples is a consequence of some inherent sluggishness. With these assumptions, the data on Madagascar microcline could be used to conclude that the microcline $\rightleftarrows$ sanidine inversion temperature ($T_c$) is not above approximately 500°C.

This conclusion is, however, open to criticism on other grounds. The nature of the hydrothermal conversion microcline $\rightarrow$ sanidine permits the possibility of an ambiguous interpretation. As earlier pointed out, the original microcline structure does not under hydrothermal conditions merely undergo a diffusive[1] transformation to sanidine as it does when heated dry at $>1000$°C. The conversion might be looked upon as *a hydrothermal synthesis of sanidine, the microcline acting as source material.* The high pressure $H_2O$ phase dissolves some of the microcline.[2] The material in solution should be, under ideal conditions, in equilibrium with whatever phase is stable at the temperature of the experiment. If below the inversion range, the solution should be in equilibrium with microcline, if above it, with sanidine. Equilibrium implies constant interchange between the solute and the material dissolved in the solvent, with equivalent amounts being transferred in either direction. However, microcline has never been synthesized. Sanidine is always produced, even at temperatures well below 500°C. A detailed discussion of this point and others relating to similar difficulties of mineral synthesis is presented by Goldsmith (1953). Monoclinic K-feldspar is the common form produced authigenically in sediments, obviously at earth-surface temperatures and in the stability field of microcline. The two-way transfer that continuously takes place in the system investigated here therefore may redeposit material from solution only in the form of *sanidine. This mechanism, if operative, could result in the production of a metastable modification* (in this case sanidine) *from a stable modification* (in this case microcline) *in the stability field of the stable modification.* Thus, it is conceivable that microcline could be hydrothermally converted

[1] See Laves (1952, p. 438).

[2] The data of Morey and Hesselgesser (1951) show that at 500°C the composition of the material in solution in superheated steam is quite close to the theoretical composition of microcline.

to sanidine *below* the true inversion temperature. This mechanism might be called a reversive (metastable) conversion.[1]

The rate or magnitude of the suggested mechanism is not evaluated here. It might, however, be reinforced by the internal stresses present in microcline as a consequence of fine combination twinning. The possibility of the reversive conversion casts some doubt on the reliability of determining inversion temperatures of certain substances under conditions similar to those here described.

Some further observations on hydrothermally treated crystal fragments are of interest. Sanidine from Vesuvius was held 3 days at 800°C (8000 lb/in.$^2$ $H_2O$), as was an adularia (valencianite) from Mexico. The fragments were observed under the microscope and the surfaces were seen to be covered with tiny (oriented) overgrowths. Thus recrystallization is apparent, even when sanidine or adularia is the source material. The amount of material redeposited in these cases, however, appears to be less than was observed on similarly treated microcline fragments, earlier described. In runs of 7 days at 595°C, this surface recrystallization could not be detected (using the same microscopic technique) with either the Vesuvius sanidine, or the Madagascar microcline.

One feature of the conversion behaviour of the Madagascar microcline might be considered as favouring an inversion temperature ($T_c$) of approximately 500°C. As seen in Table 5, appreciable conversion was observed at 525°C in 24 hours; at 500°C, no conversion was visible in 500 hours. One must consider, however, that the amount of sanidine formed at 500°C may merely be outside the limits detectable by the x-ray technique. The time element has also been shown to be not too important, especially at low temperatures. Additional experiments, on uniformly sized powder, and with quantitative intensity measurements of sanidine content are necessary.

## COMPARISON OF THE CONVERSION BEHAVIOUR OF NA-FELDSPAR AND K-FELDSPAR

TUTTLE and BOWEN (1950) converted low-temperature albite (Amelia, Va.) to high-temperature albite by a hydrothermal process essentially identical to that used here for microcline. A sodium disilicate solution was used as a flux. They noted that the change was essentially complete in 3 days at 775°C, and in 2 weeks at 720°C, but no change was observed in 3 weeks at 675°C. They state, "These results indicate that the inversion may be near 700°C. However, there is no assurance that longer heating at lower temperatures will not cause transformation, and a definite value for the inversion temperature cannot be regarded as established."

[1] This type of conversion, which at first sight appears to contradict thermodynamic considerations, is conceivable under certain circumstances. The difference in solubility of the two modifications should be small, otherwise the solvent would become distinctly supersaturated with respect to the low-temperature phase (microcline), and thus the process would essentially stop after some finite amount of sanidine had formed, as no further solution of the microcline would occur. If in the course of the experiment concentration fluctuations in the solvent are produced that are comparable in magnitude to the difference in solubility of the two modifications, the process can go on. Other important but unevaluated factors that might effect the real energy levels of the two forms and therefore shift the inversion temperature from that of the "ideal" temperature are their surface energy relations against the solvent and their state of crystalline imperfections. For example imperfections in microcline might make sanidine the stable form at a temperature below that of the inversion for ideal crystals.

The mechanism of the low-high-albite (or albite-analbite) inversion might be expected to be the same as described for microcline-sanidine. The same objections to the use of the 500°C value for microcline-sanidine might therefore also be applied to the 700°C value for albite-analbite. Nevertheless, to produce a change in the case of albite[1] higher temperatures are required than for microcline. Powdered Amelia albite was treated hydrothermally (without flux other than the $H_2O$) for 3 days at 750°C; only very slight conversion to analbite was observed. Table 4 shows that all of the microclines run at 750°C show very considerable conversion (over 70%) in less time. This difference in behaviour is undoubtedly real, and cannot be easily attributed to a difference in solubility of the two substances. Morey and Hesselgesser (1951) measured the solubility of Amelia albite and a microcline from Quebec in high pressure steam at 500°C. Albite was run at 400, 1000, and 2000 bars pressure; microcline at 1000 and 2000 bars. No essential difference in the solubilities of albite and microcline is indicated in the data of Morey and Hesselgesser.

The alkali feldspar phase diagram proposed by one of us (Laves, 1952) showed a horizontal temperature line at 700°C for the inversion of the alkali feldspars. This value of 700° was based on the albite inversion determination of Tuttle and Bowen, and on estimates in the literature for microcline, combined with crystal-chemical reasoning for the microcline-albite series. On the basis of the hydrothermal evidence now on hand, the inversion temperatures should be indicated as increasing from the potash to the soda end of the diagram, although the configuration of the curve itself is still unknown. If one accepts the hydrothermally determined value of 700°C for the albite-analbite inversion, a lower value must be taken for the microcline-sanidine inversion; at least one sample of microcline is converted in part to sanidine at temperatures down to approximately 500°C even without the use of a flux other than water.

## Conclusions

The existence of intermediate states between microcline and sanidine further strengthens the concept of Al-Si order-disorder relations between these two polymorphs. These states have been produced by dry heating of microcline (under non-equilibrium conditions) and have been observed in natural potash feldspars. Attempts to produce intermediate states *under equilibrium conditions* either by synthesis or by heat-treatment of microcline or sanidine have been unsuccessful, as have been attempted syntheses of microcline. These results can be explained on the basis of insufficient time available for experimentation in the equilibrium temperature range. It thus appears unlikely that the determination of the microcline-sanidine equilibrium relations (as diagrammatically shown in Fig. 4) can be accomplished by direct methods.[2]

Nevertheless, microcline has been partially converted hydrothermally to sanidine at a temperature as low as 525°C. Different microclines behave quite

[1] From Amelia County, Virginia.
[2] i.e., by direct inversion to a stable state at an equilibrium temperature.

differently, however, and only one (from Madagascar) was observed to show some transformation at a temperature this low in the times used. In addition, the mechanism of conversion is such that doubts are cast on the validity of assuming that the lowest temperature at which hydrothermal production of sanidine is observed is of necessity in the stability field of sanidine. The albite-analbite inversion can be considered from a similar point of view, but the data on hand suggest that the microcline-sanidine inversion takes place at a lower temperature than the albite-analbite inversion.

The difficulty of interpreting the hydrothermal data in this system makes supplementary information relating to the inversion desirable. Perhaps most valuable would be careful measurements of solubility on the two modifications at elevated temperatures. Neglecting intermediate states, the solubility curves of microcline and sanidine would cross at the inversion temperature. Measurements on intermediate states might add information on the range of temperature over which the intermediate states are stable. It is also of course, desirable to obtain thermodynamic data on the polymorphic forms. Additional hydrothermal work on the conversion would also be of value, using carefully controlled grain size (surface vs. volume considerations), quantitative measures of amount of conversion vs. time and temperature, and with carefully selected samples in the attempt to minimize differences due to composition, internal stress, etc.

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# Geochemical work of the Geochemistry and Petrology Branch U.S. Geological Survey*

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ABSTRACT

The current geochemical work of the Geochemistry and Petrology Branch of the U.S. Geological Survey is outlined under the headings of geochemical compilations, laboratory projects, and field-laboratory projects. Some thirty-seven active projects are described. Six others are mentioned which are planned for the near future. The importance and value of cooperative projects and the "team approach" are emphasized. The hope is expressed that more such projects can be undertaken; also, that summaries of geochemical work under way elsewhere will be published soon for the advancement and better coordination of geochemical research.

## 1. INTRODUCTION

About ten years after the United States Geological Survey was founded Congress authorized the Survey to undertake "chemical and physical researches relating to the geology of the United States." This was an eminently wise provision as much of the geologic work depends on and is nourished by research in the general fields of chemistry and physics, which of course today include geochemistry, spectrography, nuclear chemistry and others. The Geochemistry and Petrology Branch of the Geologic Division of the Survey has the responsibility for research in this diverse group of disciplines. As a consequence of this range of disciplines the Branch has brought together specialists in various branches of the sciences of chemistry and physics, spectrography, x-ray analysis of crystal structure, mineralogy, petrology, and field geology. It is therefore possible within the Branch, as well as by co-operation with other units of the Survey, to apply the "team approach," by which representatives of various appropriate disciplines are brought together and pool their experience for a concerted attack on a specific problem. This method of attack has met with signal success in many company and privately endowed research laboratories in the past few years.

In the early days before the team approach was given much thought great strides in geochemistry were made by a relatively few individuals in the Geological Survey. HILLEBRAND (1907), for example, laid the foundation of modern silicate analysis, which has provided so many of the raw data on the geochemistry of the lithosphere. DAY and ALLEN, working in a Survey laboratory, started the programme that developed into the Geophysical Laboratory, which has done more than any other laboratory, institution, or organization in the world to further physico-chemical research in petrology. CLARKE'S remarkable *Data of Geochemistry* (1924) has formed the basis for a great part of the modern speculation, research, and interpretation in the field of geochemistry.

It is becoming increasingly difficult for a single individual to carry out an important research programme alone. The Survey, therefore, is encouraging not only the collaboration of teams in its own laboratories, but also the sharing of problems with other groups.

* Publication authorized by the Director, U.S. Geological Survey.

The laboratories of the Geochemistry and Petrology Branch must necessarily do a great deal of routine analytical and determinative work for the important part of the Survey's programme that is geared to the search for raw materials. It must be realized, however, that, as in other fields of science, methods needed 5, 10, or 15 years hence must begin their development now. For this and other reasons the Geochemistry and Petrology Branch is making a strenuous attempt to devote at least 50 per cent of its efforts and resources to fundamental research in methods, techniques, interpretations, development of theories, and other aspects of geochemistry and related disciplines.

## 2. Geochemical Compilations

In any research job the first task is to find out what has already been done. This means a search and evaluation of the literature, whether or not this part of the work is prepared for publication. Extensive compilations of data and literature, therefore, are of great value in research programmes.

The U.S. Geological Survey has published such compilations in the past; these are being actively revised and brought up to date and other similar compilations are being prepared.

*The Data of Geochemistry* (Clarke, 1924) has long been the Survey's "best seller." It is still in demand; the last edition has been kept in print continuously for almost 30 years, and nearly 60,000 copies have been sold. Many inquiries are being received for information as to when it will be revised. It is badly in need of revision, of course, both for bringing up to date the subjects treated in the 1924 edition and for incorporation of new subjects. For example, the geochemistry of radioactive elements is hardly touched in Bulletin 770, and natural variations in the abundances of nonradiogenic isotopes are not even mentioned.

Work has been in progress on the revision for several years, but the pressure of other tasks has prevented its completion. So much geochemical information has accumulated in the past thirty years that it would be impossible for a single individual to do what Clarke did from 1908 to 1924. It will now be necessary to have a battery of experts sorting, selecting, and writing to produce a well-rounded, complete, and moderately up-to-date revision, with one individual, or a small group, responsible for the preparation of each chapter.

In the meantime references and data are being collected on punch cards in such a manner that the data in the literature on any element or any coded subject, of which there are 76 on the cards at present (such as, geological time, meteorites, the atmosphere, carbonate sediments), can be quickly segregated and assembled. A summary of recent estimates of the abundance of elements in the earth's crust has just been prepared. (Fleischer, 1953.)

It is planned to publish summary reports on the geochemistry of several individual elements,* such as germanium, gallium, indium, and niobium, and to circulate them widely with requests for criticism, comments, and suggestions.

* Similar reports, prepared for the Manhattan Project in 1945, were revised in 1946 and reproduced by the A.E.C. in the following reports:

| | |
|---|---|
| MDDC-643, Be | MDDC-645, Ge |
| MDDC-644, Nb and Ta | MDDC-646, In |

The replies to these requests, combined with the answers to a more general questionnaire that was sent out some time ago, should aid materially in shaping the framework for the new edition. A very tentative table of contents for the new edition can be obtained from the writer; comments and suggestions about it will be most welcome.

*Chemical Analyses of Igneous Rocks* (Washington, 1917) has been, since its publication, the primary source of information for all those working on the chemistry of individual rock types and rock groups. A great deal of excellent analytical work has been done on igneous and metamorphic rocks since that time; summaries of analyses from individual laboratories and of rocks from various countries have been published, but no general compilation has been made.

The Geological Survey has begun the work of revising Professional Paper 99 and extending it to include analyses of metamorphic rocks. It will include selected analyses of igneous and metamorphic rocks published from 1884 through 1953, together with computations of the norms and Niggli numbers for all superior analyses.

This project also requires a trained team—to search the literature, select the analyses, calculate the norms, and arrange and index the information so that it can be used in as many ways as possible.

After publication of the analyses for the period 1884–1953 we hope to keep the files as a continuing, growing, and useful adjunct to international petrologic work, containing not only all published results but as many unpublished analyses as possible. If all results could be sent promptly for incorporation in the central files then a geochemist or a petrologist anywhere in the world, by writing a single letter of inquiry, could find out whether there were any analyses of a given rock type or of rocks from a given area, published or unpublished.

*Nonradiogenic isotopes in geology.* Variations in the ratios of nonradiogenic isotopes of various elements in nature have been recognized only comparatively recently. Many papers on this subject are now appearing each year, but compilation of all the work done thus far in this field does not compare in magnitude with either of the other compilations mentioned above.

Such a compilation, essentially complete through 1952, has recently appeared (Ingerson, 1953). In addition to summarizing the work already done, this paper also outlined the physical, chemical, and biological processes that are, or might be, effective in natural isotopic fractionation and suggested situations in which such separations should be sought and geologic interpretations that could be made if determinable separations are demonstrated in these situations.

A file of reprints and references on the distribution of nonradiogenic isotopes in nature is being maintained in the Geochemistry and Petrology Branch and when sufficient data have accumulated it is planned to rewrite the review, incorporating all of the data available at that time.

*Radioactive and radiogenic isotopes in geology.* A similar review is in preparation in the Branch on radioactive and radiogenic isotopes in nature. Much of this information is incorporated in the annual reports of the Committee on Geologic Time of the Division of Geology and Geography of the National Research Council. From these reports it is difficult to summarize what is known of the distribution

of the isotopes of a given element because (1) many other subjects, such as analytical chemistry of radioactive elements, properties, and occurrences of radioactive minerals, are included in them and because (2) it is now necessary to go through some eighteen separately bound reports to cover the period 1932–1952. For these reasons it will be convenient and worthwhile to have all the information on isotope distribution for these elements summarized in a concise yet comprehensive review.

*Hydrothermal synthesis and alteration of minerals.* In 1937 (Morey and Ingerson) a complete summary was published of the experimental work on the hydrothermal and pneumatolytic synthesis and alteration of silicates that had appeared before that time. A relatively brief introductory section outlined the theoretical considerations behind the experimental work and suggested certain cautions and interpretations.

A cooperative project between the Geophysical Laboratory of the Carnegie Institution and the Geological Survey proposes to revise and extend this compilation. The introductory material will be completely rewritten and expanded into a comprehensive treatise on the theory and practice of experimental hydrothermal work. Abstracts are being prepared of post-1937 work on silicates and all the experimental hydrothermal work that has ever been done on the other groups of minerals. All the material will be combined, arranged chronologically, and indexed thoroughly.

## 3. Laboratory Projects

### *Analytical Laboratories*

The analyst is the backbone of almost any geochemical project. If it were not for his repetitive determinations there would be very little geochemical data to analyze and interpret.

The Geochemistry and Petrology Branch maintains nine regular analytical groups, besides smaller units working on specialized techniques on the chemistry of individual elements for which current methods of determination are not satisfactory, and doing analytical work for research projects. In these nine groups there are approximately 70 chemists and spectrographers. They handle some 75,000 samples per year and make about 400,000 individual determinations on them. In addition to these determinations most of these nine groups carry out a considerable amount of research work to improve the techniques they are using.

These numbers do not mean a great deal because they involve so many kinds of determinations that differ so much in nature, complexity, and amount of time required. Figures for individual laboratories, or groups of laboratories doing similar work, are more significant. These are summarized below.

*Rock analysis laboratory.* In Denver, Colorado, the Branch has a laboratory devoted to rock analysis by conventional methods. Currently there are five chemists in this laboratory. Their work consists mostly of complete analyses of rocks, of which they turn out approximately 500 per year.

*Analytical laboratory, Washington.* A laboratory somewhat similar to the Denver one is maintained in Washington. Very few complete ordinary rock analyses are done in this laboratory, however, its work being largely analysis of difficult samples such as mineral analyses involving very small amounts of material,

determination of rare or difficultly determinable elements, or tedious problems of mineral separation. On occasion satisfactory analyses of new minerals have been obtained with as little as 5 mg of sample. This group now consists of five chemists and they make some 2000 determinations per year on approximately 250 samples.

*Rapid analysis laboratory.* There are many kinds of geological and geochemical problems for which a large number of approximate analyses are worth more than a few accurate ones. For this reason the Geochemistry and Petrology Branch started several years ago to develop methods that would speed up analyses several-fold and yet would have the accuracy required for most geological work. Actually the accuracy approaches that of conventional methods, but one operator can analyze approximately 10 silicate rock samples in a five-day week. The first methods developed are outlined in Geological Survey Circular 165* (Shapiro and Brannock, 1952). These methods have been improved and new ones added; a revision of the circular is in preparation.

The Rapid Analysis Laboratory has seven chemists making some 12,500 determinations on approximately 1050 samples per year, besides continuing research on methods. (Two of the seven chemists are working on research.)

*Analyses for A.E.C. raw materials programme.* Under contract to the Atomic Energy Commission, the Geological Survey maintains two laboratories, one in Washington and one in Denver, for analysis of samples in connection with the radioactive raw materials programme. A great deal of the work, of course, is determination of uranium, but a comparable number of determinations of other associated elements are also made each year. There are thirty chemists in the two laboratories making some 60,000 determinations per year on a total of about 30,000 samples.

*Spectrographic laboratories.* The Branch maintains three completely equipped spectrographic laboratories, two in Washington and one in Denver. There are a total of sixteen spectrographers in these laboratories, and they make approximately 300,000 determinations per year on a total of some 30,000 samples.

A spectrographic technique that gives a good result on one rock or mineral may yield a completely erroneous figure for a different kind of material. An operator in a spectrographic laboratory that analyzes geological materials, therefore, must constantly be alert to employ the proper techniques and standards for the types of materials that he is analyzing. The laboratories of the Survey have these problems very much in mind and have worked out procedures for determining 69 elements, with limits of detection ranging from 0·0001 to 0·1 per cent.

*Geochemical prospecting* is a combined laboratory-field project, but the Geochemistry and Petrology Branch has responsibility only for the laboratory part. The tests used are still in the developmental stage, and three chemists are spending full time in devising and improving tests for various elements.

Satisfactory tests are now available for Cu, Pb, Zn, Ag; Co, Ni, Mn; Mo, W, Nb; As, Sb; and methods are being perfected for Se, Sn, and Ge. The methods used are described in Geological Survey Circular 161 (Lakin, Almond, and Ward, 1952).

* These Survey circulars are available, free of charge, on application to the Director, U.S. Geological Survey, Washington 25, D.C.

In another laboratory (both are in Denver) four other chemists do the service work for the geochemical prospecting field projects. They make approximately 22,000 determinations on 12,000 samples in the course of a year. Most of the tests are designed so that they can be performed in the field with simple kits. During the field season some of the chemists accompany field parties and make the tests on the ground, which greatly speeds up delivery of results to the geologist, and thereby his interpretations.

A complete mobile spectrographic laboratory is being installed in a truck for use by the Geochemical Prospecting group. It will be powered by a motor-generator unit mounted on a trailer. It should be possible soon for field parties to have on-the-spot spectrographic as well as chemical determinations.

The finding of ore by geochemical methods is the function of the geologist (Mineral Deposits Branch, in the Survey), but it may be of interest that recently a stibnite deposit was located at Camaano Point, Alaska, where the Tillicum Mining Company is carrying out an exploration programme under Defense Minerals Exploration Administration. The discovery was made entirely on the basis of geochemical prospecting tests for antimony on soil samples from a layer of muskeg and matted roots 2 to 5 feet thick. The cover was so complete and extensive that there was no reason to suspect the presence of the deposit from geological considerations.

*Precision and accuracy.* In connection with its analytical programme the Branch has a project on precision and accuracy of results. Its studies are theoretical; its aims are to evaluate the precision and accuracy of our analytical results and to help increase them where such improvements are necessary or desirable.

Cooperation of this group, the Geophysical Laboratory, and the Department of Geology of Massachusetts Institute of Technology produced the comprehensive study of the results of analyses of two standard rocks (a granite and a diabase) by a large number of analysts, that has recently appeared as Bulletin 980 of the U.S. Geological Survey (Fairbairn *et al.*, 1951). This group also sends samples of the granite and diabase to analytical laboratories on request and maintains records of their results.

*Synthesis of data.* One of the big problems of the Geochemical and Petrology Branch now is how to integrate and interpret the tremendous amount of data that are accumulating year by year. Analyses are made for dozens of projects. Each project leader takes and interprets the data for his samples, but the problem of combining and interpreting all of the data, even for a single element, is very much more difficult. An attempt is being made to do this for uranium; for the other elements as complete summaries as possible will be incorporated in the reports and chapters on these elements which are to be prepared in connection with the above-mentioned revision of the Data of Geochemistry.

### *Special Techniques; Certain Elements*

From the summaries of the work of the various laboratories it is evident that the Washington analytical laboratory turns out fewer determinations per man year per year than any of the others except the conventional rock analysis laboratory, There are several reasons for this. One of the most significant is the fact that

many of the analyses are for unusual elements, the chemical determinations of which are tedious and slow. For this reason new and promising techniques for the determination of such elements are under investigation.

*Polarography.* Where it is desired to determine a small amount of one metal in the presence of large amounts of other metals, polarographic methods are particularly time saving. Metals such as Cu, Pb, and Zn are readily determined, and recently a method for tungsten has been perfected. After the material is in solution the determination requires about 10 minutes, as compared with several hours for the chemical method.

*X-ray fluorescence.* For certain elements near the centre of the periodic table that give a great deal of trouble in chemical determinations, and even some that are difficult to determine spectrographically, x-ray fluorescence promises to give rapid and accurate analyses. The determination of niobium has always been a problem. Wet chemical determinations require days; preliminary separation of Ta and Nb and subsequent spectrographic determinations require some hours. With x-ray fluorescence one man can prepare 50 to 60 samples in one day and determine them the next, an average of more than 25 samples per day. Techniques for Se and perhaps Ge will be worked on next.

*Analytical chemistry of thorium.* In recent years the U.S. Geological Survey has become more and more interested in the thorium content of rocks which contain trace amounts of this element. None of the reagents for thorium described in the literature were sufficiently sensitive to be used conveniently for the analysis of extremely low grade ores. A project was therefore initiated to find a reagent which would be highly sensitive, and if possible selective for thorium.

The investigation is still in its early stages, but a reagent has been found that gives both a colour and a fluorimetric reaction. This reagent appears to be very promising as a basis for the quantitative determination of thorium. It is believed that about 0·2 microgram of $ThO_2$ per 50 ml of solution can be determined with this reagent.

*Determination of uranium.* Work for the A.E.C. demands that large numbers of uranium determinations be made on materials with greatly different uranium contents. Three kinds of techniques are used for various purposes as follows:

(1) All samples for radioactive raw materials reconnaissance and exploration are first scanned *radiometrically.* Those showing more than 0·01% equivalent uranium have their uranium contents determined; (2) *chemically* (reduction followed by oxidation with $KMnO_4$). (3) For determination of very small quantities of uranium specialized *fluorimetric* techniques have been developed. Both reflection and transmission fluorimeters are employed. Two methods are used to eliminate or reduce interference by other elements. (a) Where the interfering elements are present in small enough amounts the "dilution" method can be used. This consists merely of taking such small samples of the mineral that the interference is insignificant. The degree of quenching depends only on the concentration of quencher in the flux, and not on the ratio of concentration of quencher to concentration of uranium. (b) In determining extremely small amounts of uranium or when too much of interfering elements is present it is sometimes necessary to separate the uranium from the other elements before the flux is

prepared. With extreme care amounts of uranium as small as $10^{-9}$ gram per gram of sample can be determined in some types of material by this method.

Fluorimetric methods can also be used for materials with larger quantities of uranium, even uraninite, but as the error is about 5% of the amount present chemical determination is used where greater accuracy is required on samples that contain more than a few hundredths of a percent uranium. The Survey's fluorimetric methods are described in Circular 199 (Grimaldi, May, and Fletcher, 1952).

### *Mineral Synthesis*

Synthesis of minerals, either as a part of a system that is being studied systematically, or isolated runs under varied conditions, can be useful in geologic thermometry by indicating ranges and areas of stability of individual minerals or mineral associations.

Laboratory growth of minerals can also aid in solving other problems such as (1) determining the properties of a mineral that does not occur sufficiently pure or in large enough quantities in nature for a good determination, (2) finding out how a given element occurs in a certain mineral and determining what conditions favour its inclusion or exclusion, and (3) properties and interpretations of solid-solution series.

Current work in mineral synthesis in the Geochemistry and Petrology Branch is largely limited to three systems: (1) The system $K_2O$-$V_2O_5$-$UO_3$-$H_2O$ is being investigated at atmospheric pressure and temperatures below 100°C. (2) The system $Na_2O$-$ZrO_2$-$SiO_2$-$H_2O$ is being investigated hydrothermally at temperatures up to 525°C. (3) The system CaO-$P_2O_5$-$H_2O$ (with minor amounts of $UO_3$) is being studied hydrothermally up to 500°C.

## 4. Field-laboratory Projects

### *Geochemistry of Uranium*

As indicated above the Geochemistry and Petrology Branch is interested in the geochemistry of all elements; this interest will culminate in the revision of the *Data of Geochemistry*. It is not possible, of course, for one group to be working in the experimental geochemistry of all of the elements simultaneously, so our active work is confined to a few elements which are important for one reason or another just now. At present more effort is being devoted to the geochemistry of uranium than to that of any other element. The work can best be described by sketching several specific projects:

The distribution of uranium in igneous rocks:

#### (a) In intrusive complexes

An extensive study of the distribution of uranium in several igneous complexes of widely different geologic age and geographic location is under way. The following generalizations have been deduced:

(1) The concentration of uranium in a given type of rock varies from one part of the country to another; in other words, it is dependent upon the petrographic province in which a series occurs. For example, granites from the southern

California batholith contain 3 to 6 ppm of uranium, whereas those of the White Mountain plutonic volcanic series in New Hampshire contain 12 to 14 ppm.

(2) In a given series the uranium increases progressively toward the granitic end. Gabbros from the southern California batholith contain 0·1 to 0·3 ppm of uranium; the granites, 3 to 6 ppm.

(3) In a given rock the uranium content of the individual minerals differs tremendously. Uranium is concentrated mainly in the accessory minerals, especially zircon. For example, a granite and a diorite from the southern California batholith, whose uranium contents are 3·2 and 1·8 ppm, respectively, show the following concentrations in ppm in the separate minerals:

| *Minerals* | *Granite* | *Diorite* |
|---|---|---|
| Quartz and perthite | 1·1 | 0·6 |
| Plagioclase | 6 | 2·2 |
| Biotite, hornblende, and pyroxene | 9 | 3 |
| Magnetite | 10 | 7 |
| Allanite | 35 | |
| Zircon | 8600 | 1040 |
| Sphene | | 350 |
| Apatite | | 37 |
| Epidote | | 15 |

(4) Minerals from granitic rocks have higher concentrations of uranium than the same minerals from lower silica rocks of the same series, as shown in the above tabulation.

### (b) In extrusive rocks, especially volcanic ash

It has long been held in certain quarters that much of the energy released in volcanic eruptions, especially during the early stages, is produced by abnormal radioactivity in the magma. The fact that some lignites that are higher than normal in uranium are associated with altered volcanic ash (bentonite) has been interpreted by some as supporting that idea. The study of uranium in extrusive rocks has not progressed as far as that on intrusives, but thus far no example of a fresh pyroclastic rock or flow has been found in which the uranium content is higher than would be expected in an intrusive rock of the same composition. For example, three samples of pumice from the July 29, 1952, eruption of Kilauea, two from the September 13, 1952, eruption of Myojin Reef, Tokyo Bay, and two from the July 9, 1953, eruption of Mt. Spurr, Alaska, were analyzed for uranium. All of them showed less than 0·0005% U. The inference is that in the example mentioned above the uranium was either leached from the lignite and adsorbed by the bentonite, or was added to both by later uraniferous solutions.

### (c) In bostonite dikes and related veins

In the Central City Mining district, Colorado, a detailed study of bostonite dikes

and related pitchblende-bearing veins is being made. The bostonites contain up to 20 times as much uranium as the average granite. Results thus far indicate that uranium-rich solutions given off by a cooling quartz bostonite mass at depth became further enriched by leaching uranium from the bostonite in and near the channelways. In other words, uranium-bearing veins are associated with a bostonite dike, or parts of one, *low* in uranium.

If it can be shown that this relationship is general and that it applies to other elements, these studies may have an important bearing on our ideas of ore formation and, consequently, on the methods of prospecting for certain types of deposits. Details of this study are given in the Survey's Trace Elements Investigation Report No. 247 (PHAIR).*

*Weathering, transportation, and deposition of uranium.* A study of the influence of *p*H and oxidation potential on the weathering and transportation of uranium is under way. So far the principal application has been to the Colorado Plateau type ores. It appears that the high-valence uranium and vanadium compounds that are commonly found near the surface (carnotite, tyuyamunite, etc.) are stable under oxidizing conditions and are derived by weathering of the low-valence compounds which are stable under reducing conditions and which are commonly encountered at greater depths in mines and drill cores than those at which the higher valence compounds are found.

*Uranium in phosphates.* It has long been known that marine phosphates are higher in uranium than most other types of sedimentary rocks. The Geochemistry and Petrology Branch is studying phosphates from several different fields in an attempt to answer the following questions: Why is there an abnormal uranium content in marine phosphates? Where is it concentrated; in certain zones, or certain minerals, or both? Why is it thus concentrated? What is the range of concentration? Is it approximately the same in all phosphate fields? In different parts of the same field? Is there a relation between uranium content and $P_2O_5$ content? Between uranium content and the content of other trace elements?

Satisfactory answers have been obtained to some of these questions; tentative answers to others and no answers to still others.

*Uranium in carbonaceous and related rocks.* At least three separate projects are under way in this programme: (1) Uranium in lignite and coal, (2) uranium in asphaltite and petroleum, and (3) uranium in black marine shale. Answers to questions similar to those asked about the phosphates are being sought. These problems have been studied for a long time in many places with scant results. The Geochemistry and Petrology Branch is applying a new approach that might be called "organic geochemistry." It involves (1) separation of the organic compounds, or at least components, (2) determination of the structure of the organic matter, and (3) determination of the relation of the organic material to the trace elements it concentrates.

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* PHAIR, GEORGE (1952): Radioactive Tertiary porphyries in the Central City district, Colorado, and their bearing upon pitchblende deposition; U.S. Geol. Survey Trace Elements Inv. Rep. 247, 53 pp. (open-filed by the U.S. Atomic Energy Commission, Technical Information Service, Oak Ridge, Tennessee).

This approach has demonstrated that the uranium in coal is not associated with the minerals, but is contained in an organic-uranium complex. Similar studies are being made of black shales and asphaltites, but these materials offer greater difficulties.

### *Other Minor Elements in Coal*

For this study columnar samples of numerous coals from fields both in the western and eastern United States have been collected. Columnar samples have the advantage of telling *where* in the coal bed concentrations of minor elements occur. Data are available in rough form on 15 minor elements (Ga, Be, Ti, V, Cr, Cu, Sn, Zn, Ni, Co, Mo, Y, La, B, and Ge), but they have been collected into report form only for germanium.

The highest concentrations of Ge found thus far, up to 7·5% Ge in the ash, are in coalified logs and pieces of woody coal isolated in sediments. The richest commercial coal found so far is the bottom horizon of the Lower Kittanning coal of Pennsylvanian age in Ohio. The ash of this coal contains 0·2% Ge. The Ge is commonly concentrated in the top and bottom layers of coal beds. Ge tends to concentrate in the bright woody coal (vitrain) and is low in fusain (mineral charcoal). There is no detectable concentration in pyrite or sphalerite. Simple gravity separation of crushed germaniferous coal can produce fractions high in woody coal, the ash of which has 2·5 times as much Ge as the ash of the original coal.

There appears to be a regional variation in the amount of Ge in coals. The coals in the eastern states contain more Ge than the same kinds of coals of the western states.

Details of the study of germanium in American coals are given in Geological Survey Circular 272 (Stadnichenko *et al.*, 1953).

### *Geochemistry of Niobium*

Niobium in rocks occurs in highest concentrations in granitic pegmatites and in alkalic rocks such as nepheline syenites. A co-operative project is under way to make a detailed study of the Nb content of the various rock types, of the minerals in these rocks, and of the associated vein minerals at Magnet Cove, Arkansas. Detailed study of a small alkalic intrusion and associated carbonatite at this locality may suggest where to look for the greatest concentrations of Nb in similar complexes elsewhere.

The niobium occurs commonly as a substituent in titanium minerals. Preliminary results indicate that at Magnet Cove brookite contains more Nb than rutile, and perovskite, more than brookite. The titanium minerals in the carbonatite contain more Nb than the same minerals in the syenite.

Preliminary results of the niobium project are given in Geological Survey Circular 225 (Fleischer *et al.*, 1952).

### *Geochemistry of the Rare Earths*

An emission spectrographic method for accurately determining the individual rare-earth elements in cerium minerals has been developed and is being used to

study the geochemical factors that control the distribution of these elements. The method was first applied to monazite samples from 10 localities widely separated throughout the world. When individual elements are plotted against the sum of La, Ce, and Pr, praseodymium is nearly constant at 5 atomic per cent; lanthanum and cerium increase more or less regularly as the sum of La, Ce, and Pr increase, whereas neodymium and the sum of samarium, gadolinium, and yttrium decrease in a similar fashion.

Fractional crystallization during the formation of rocks leads to an increase in the sum of La, Ce, and Pr so that higher concentrations of these elements represent later stages of differentiation, whereas Nd, Sm, Gd, and Y decrease relative to La, Ce, and Pr as differentiation proceeds. Deviations from straight lines are believed to reflect differences in temperature of crystallization of the various monazite samples for the stage of differentiation reached.

### *Geochemistry of Pacific Rocks*

The Geological Survey is encouraging and taking part in a long-range programme to increase and coordinate knowledge of the geochemistry of the rocks of the Pacific Basin. The following groups are actively co-operating in the study:

(1) The Volcano Unit of the General Geology Branch has supplied samples from the Hawaiian and Aleutian Islands and has helped in the collection of other samples from Hawaii. They have also supplied material to

(2) L. R. Wager and R. L. Mitchell, who have studied the minor-element content of a series of Hawaiian rocks and compared them with similar studies of lavas from the Isle of Skye and of rocks of the Skaergaard Intrusion, East Greenland.

(3) The geologists of the Tokyo office of the Military Geology Branch have had analyses made of volcanic rocks of the Palau Islands and have supplied samples from some of the volcanic centres of Japan.

(4) The Guam Geological Survey has aided in collecting samples from Guam and has supplied additional samples from Guam and other islands of the Marianas Group.

(5) The geochemical group at California Institute of Technology has been supplied a considerable number of large samples from some of the areas mentioned above. Their interest is primarily in the abundance and isotope ratios of Pb, U, and Th; the purpose is to gain knowledge of the geochemistry of uranium and thorium, but they hope to develop a technique for determining the age of many more rocks by the lead-uranium method than can be so determined at present.

Among the general objectives of the programme the following may be mentioned:

1. Comparison of general chemical characteristics of rocks of different areas of the Pacific. Are there areas comparable to "metallogenic provinces" of continental areas? For example, are rocks of some areas characterized by higher copper, chromium, or vanadium content than comparable rocks of other areas?

2. If such areas exist is there a geographic trend to the variations, or are they irregular?

3. In a given group of islands, such as the Hawaiian chain, it is planned to make the following comparisons of major and minor element contents:

(a) Similar rocks of approximately the same age from as many different centres of activity as possible.

(b) Similar rocks of different ages from the same centre and from different centres. Studies of this kind have already been published for some Hawaiian rocks, both for major (MACDONALD, 1949a and 1949b; STEARNS and MACDONALD, 1946) and minor (WAGER and MITCHELL, 1953) constituents. Both sets of results are in conformity with the view that the Hawaiian rocks are essentially the result of fractional crystallization.

(c) A series of rocks from the youngest to the oldest available from each of several centres of activity. (All four major centres on Hawaii should be studied this way and at least one each on Maui, Oahu, and Kauai.)

In addition, the average composition of the rocks from each major centre should be estimated. These studies should make it possible to tell whether differentiation has proceeded on a regional basis at depth under the whole group of vents, or whether the same fundamental magma has been supplied to each volcano and the differentiation has taken place locally in magma chambers and conduits below each one.

4. When enough results are available it should be possible to delineate the "andesite line" more accurately and to see what relation it bears, if any, to tectonic boundaries in the Pacific.

Many more limited problems will be worked on in the course of these studies. For example, if the group at the California Institute of Technology succeeds in getting absolute age determinations on these rocks, then it will be possible to check the validity of the suggestion that $K_2O$ content is an index of stage of differentiation and therefore of relative age and the idea that BaO might serve equally well and be a check on the $K_2O$ method. Or it might be found that some other constituent is better than either. Also, it might be possible, after correlation with radioactive age determinations to use minor-element content to estimate absolute age in a given series of rocks.

### *Geochemistry of the Watchung Basalt*

The Watchung basalt flows of Triassic age in northern New Jersey are being studied in detail petrologically and geochemically. The field and petrologic studies are well along and samples have been collected for studies of variations in composition. Both major and minor constituents will be determined and the results correlated with relative ages, stage of differentiation reached, etc.

### *Geochemistry of Parícutin Lavas*

The lava flows at Parícutin are readily dated with respect to one another and the absolute ages of most of them are accurately known. This makes the situation a very interesting one for study of the change of minor-element content of the lavas with time and differentiation.

Samples covering the entire life span of the volcano have been analyzed

spectrographically for Ni, Cr, Co, Cu, V, Ga, Sc, Zr, Sr, Ba, and B. In general, the variations in the concentration of these elements with time are closely related to the variations of the major elements.

Nickel shows the largest range of variation with 0·013% in the first flow to 0·007% in the last flow. Furthermore nickel parallels magnesium in showing a rapid drop in concentration in the lavas of June to September 1947. Chromium, cobalt, and copper decrease in concentration with time but not as markedly as nickel. Elements that remain more or less constant are V, Ga, Sc, Zr, and Sr. Barium increases slightly in concentration, and detectable amounts of boron appear only in the later flows.

Minor elements in dioritic xenoliths in Parícutin lavas have also been determined and their value in explaining the mechanism of chemical change of the lavas with time is being assessed.

### *Geochemistry of Hot Springs and Geysers*

In co-operation with the Mineral Deposits Branch an intensive study of the hot springs of the Steamboat Springs area, Nevada, has been under way for several years. The source of the heat appears to be the magmatic centre that produced the recent nearby volcanic domes of pumiceous rhyolite.

A thorough chemical study of the surface and near-surface water of the area and of water from several of the hot springs indicates that the boron, sulfur, $CO_2$, arsenic, antimony, fluorine, and abnormal amounts of chlorine are probably derived from the magmatic source that supplies the heat and part of the water.

Density and isotope studies of the water suggest that the magmatic water is heavier than the stream water of the area and that in some of the hotter springs 6 to 16% of the water may be of magmatic origin. The higher temperature springs are more alkaline.

Some of the results have been summarized by Brannock *et al* (1948) and by White and Brannock (1950). The chemical studies are continuing and a similar project on the hot springs and geysers of the Yellowstone National Park is under way. It is hoped that some of the findings and the principles developed in these areas may have general application in similar areas elsewhere.

### *Geochemical Studies of Clay Minerals*

Pioneer work on clays led to an understanding of their mineralogy (e.g., Ross and Kerr, 1931). Continuing work on clays has been of a more chemical nature and has dealt largely with the effect of composition on the properties of the montmorillonites, i.e., the effect of substitutions in the clay structure on the base exchange and swelling properties (Foster, 1951 and 1953). Work on the montmorillonites is still in progress, but attention is also being given to the hydrous micas and to the relation between these and the montmorillonites on the one hand and the micas on the other.

### *Geochronologic Studies*

*Lead-uranium and lead-lead ratios.* Age determinations of the carnotite and related ores of the Colorado Plateaus by the lead-uranium and $Pb^{206}/Pb^{207}$ methods have had an important bearing on theories of origin of the ore and are affecting

exploration studies and policy. Early in the study of these ores they were interpreted as having been formed during or soon after the deposition of the enclosing sediments. These are of Late Jurassic and Late Triassic age, some 125 and 150 million years old, respectively. If a given deposit is syngenetic, then it should be limited to a given formation; if it was formed by later ascending hydrothermal solutions, ore minerals may have been deposited at any favourable location between the currently known deposits and the source of solutions. It is of utmost importance, therefore, to learn as much as possible about the age and manner of origin of these deposits. The best age determinations thus far made on the uranium deposits of the Plateau give a value of about 70 million years, indicating a Late Cretaceous or early Tertiary age. Intrusive rocks of about this age are numerous in the region; mineralogy of the deeper (unaltered) parts of some of the deposits strongly suggests hydrothermal origin. If this interpretation is correct, exploration should be carried to much greater depths than would have been considered under the original hypothesis of origin. A preliminary paper (STIEFF and STERN, 1952), and a Survey Circular on this work have been published (STIEFF, STERN and MILKEY, 1953).

"*Zircon method.*" The Geochemistry and Petrology Branch is developing a method of applying these same techniques to determining the age of almost any granitic rock by measuring the lead and uranium in the contained zircon. The lead is determined spectrographically and the uranium by alpha counting. This method has given consistent and logical results on a number of granitic rocks; for example, zircons from rocks whose ages had previously been determined gave the following results:

| *Locality* | *Previously determined age (In million years)* | *Zircon age (In million years)* |
|---|---|---|
| Renfrew, Canada | Proterozoic 1000 | 900 |
| Wichita Mountains, Oklahoma | Late Proterozoic 700 | 675 |
| Statesville, N.C. | Devonian 300 ± | 306 |
| Southern California | Middle Cretaceous 100 ± | 100 |

The method has about reached the stage where it can be released for routine determinations of this kind. The other accessory minerals of granitic rocks do not give satisfactory results. Apatite and sphene give too great an age and therefore must contain primary lead; moreover, sphene gives erratic results. The methods are described and preliminary results given in a paper by LARSEN *et al.* (1952).

*Radiocarbon studies.* Research is in progress on techniques and interpretation of $C^{14}$ age determinations. Converting the sample to a gas (acetylene) before counting has several advantages: (1) Smaller samples (2 g of carbon, as against about 8 g when counting elemental carbon) can be used, (2) contamination by adsorption of radioactive impurities on the carbon is eliminated, and (3) the geometry of the counting setup is improved.

Research on interpretation concerns such problems as (1) the wood *vs.* shell

problem, (2) possibility and evaluation of exchange with atmospheric or dissolved $CO_2$, (3) differences between marine and fresh water shells, (4) use of "old" $CO_2$ from ocean depths by marine organisms in certain situations, and (5) change of $C^{14}$ content of the atmosphere with the coming of the industrial age.

### *Chemical Oceanography*

Work in chemical oceanography has thus far been confined to two relatively narrow fields: (1) Improvement of methods of determining the metallic ions in sea water and (2) advisory service to the cooperative Saline Water Committee on methods of purification of sea water.

### *Studies of Liquid Inclusions*

*Geologic thermometry.* Liquid inclusions in natural and artificial minerals are being studied intensively in an attempt to improve estimates of the temperature of formation of certain types of deposits. Quartz is the best mineral for this purpose. Suites of quartz from pegmatites, quartz veins, and quartz gangue from ore deposits are being studied.

Artificial quartz grown under known conditions of temperature and pressure has been supplied by Signal Corps contractors. Preliminary results indicate that the fundamental assumption of liquid inclusion thermometry that the inclusions are just filled with fluid at the temperature and pressure obtaining during the growth of the crystals is justified. Temperatures at which the inclusions are just filled with fluid are determined on a heating stage and a correction applied for the known pressure of the run in which a given crystal was grown. The corrected temperature is within a very few degrees of the actual temperature of the run.

Numerous samples have been collected where other minerals are enclosed in quartz, and it is fairly obvious that the two (or more) minerals were either growing simultaneously, or so nearly so that the temperatures of deposition are essentially identical. The specimens are from widely scattered localities, mostly Brazil, Arkansas, Switzerland, and California. Among the included minerals are rutile, brookite, anatase, chlorite, actinolite, clay, feldspar, hematite, pyrite, helvite, dolomite, toumaline, muscovite, and scheelite. It is possible that some of the associations may have a fairly narrow range of formation and thus serve as useful indicators of temperature without the necessity of making a study of the liquid inclusions.

*Composition of the liquid.* A collection of quartz crystals with medium to large liquid inclusions is also available for study. Most of these are from Brazil and Arkansas. The liquids are very likely essentially samples of the solutions from which the quartz crystals grew, except that much of the contained silica no doubt deposited on the walls of the cavities as the crystals and solutions cooled. It is probable that these liquids are closely related to some ore-forming solutions and their compositions may indicate the approximate composition of such solutions, with the components of the ore minerals removed.

### *Isotope Geology*

*Theoretical studies.* The Branch is undertaking a broad programme based on the study of the distribution of isotopes in natural materials. While the instruments

were being built a theoretical study of natural processes of isotopic fractionation was completed (Bracken and Senftle, in press). Laboratory studies to check the conclusions are in progress.

*Distribution of isotopes in nature.* Two mass spectrometers have now been completed and a third one is planned. Of the two finished instruments one is designed primarily for particles with masses over 200; the other, for masses below 50. The one designed for heavy particles will be used principally, at least at first, to determine the ratio $U^{238}/U^{235}$ on uranium from as great a variety of sources as possible, and to determine the isotopic composition of lead for problems of geochronology. The other one will be used at first to determine the isotopic composition of hydrogen, oxygen, and carbon. Typical problems will include: (1) Determination of the isotopic composition of juvenile water, (2) estimates of amount of juvenile water in geysers, hot springs, perlite, etc., (3) origin of hydrous borate minerals, (4) age of glacier ice, (5) origin and history of carbonatites, and (6) temperature of formation of various minerals.

*Isotope standards.* Isotope ratios have been measured for many elements in various kinds of natural materials by numerous laboratories throughout the world. Each laboratory has adopted arbitrary standards and some of them have used different standards for a given element from time to time. With the mounting number of such determinations it is becoming increasingly difficult to correlate and compare results of different laboratories. The need is pressing, therefore, for a collection of standard samples that can be analyzed by workers throughout the world and can serve as reference points for all determinations of isotope ratios. The National Bureau of Standards, with the co-operation of the Geochemistry and Petrology Branch of the U.S. Geological Survey and the financial support of the Atomic Energy Commission, is establishing such a collection of isotope standards.

## 5. Imminent Projects

### *Laboratory of Chemical Volcanology*

Plans have been under way for five years to establish a laboratory of chemical volcanology at the Volcano Observatory, Hawaii National Park, Hawaii, T.H. The site has the advantages of (1) location on the rim of an active volcano (Kilauea), (2) ready accessibility, (3) availability of power, (4) integration with an existing laboratory, (5) relatively easy access to chemical facilities and interested personnel at the University of Hawaii at Honolulu.

Several important functions could be performed as soon as the laboratory is established. These can be divided into two groups:

*Studies of volcanic gases.* No really satisfactory method of collecting uncontaminated volcanic gases has ever been devised. This problem would be a cardinal challenge to the staff of the laboratory.

Gases (principally steam) emerge from cracks in the floor of Kilauea continuously. From the rift north of the crater (Sulfur Bank) hotter and more complex gases are given off all the time. It has been suggested that these gases change in composition before and during an eruption, but data are too sparse to support or disprove the theory. One of the first tasks of a geochemical laboratory at this

location would be to set up a system for checking the compositions, chemical and isotopic, of these gases almost continuously over long periods of time while the volcano is quiet, restless, and active.

Other properties should also be recorded over the same periods: temperature, pressure, and rate of escape. If significant variations in composition, or other properties, can be shown to take place before and during eruption, then another method of predicting volcanic eruptions will be available.

It may well prove to be impossible to collect pure samples of the gas that is given off while the volcano is very active. Even if this could be done the constitution of the gas would be changed before it could be analyzed. We should have knowledge of its ultimate composition, but not of the compounds (and elements) that were given off from the lava. It may be possible to set up a spectrograph and light source in the fire pit of Halemaumau so that the gas can be analyzed, at least for the more abundant constituents, just as it leaves the lava before it has been oxidized by contact with the atmosphere or has undergone reactions on cooling.

*Studies of solid volcanic products.* Once the geochemical laboratory is operating there will be time for rock analysis during the long periods of inactivity of the volcano. This part of the programme will be coordinated with the project on the Geochemistry of Pacific Rocks. Personnel on the ground all the time can do much more detailed studies of this kind than have been done heretofore.

### *Phase Equilibrium Studies*

A number of studies of occurrences of saline and carbonate minerals are in progress by members of the Geological Survey staff. These studies are being carried forward by ordinary field methods and analytical-descriptive laboratory studies. Phase equilibrium studies are needed for interpretive work on the origin of the deposits. Work will start on this aspect of these problems as soon as space and physical chemists with the requisite training are available.

The field projects and the corresponding systems on which work is needed are:

(1) *Carbonates of the Green River formation, Wyoming.* The system $Na_2O$-CaO-$CO_2$-$H_2O$ should be studied.

(2) *Borate deposits in basins of the southwestern United States.* The system $Na_2O$-CaO-$B_2O_3$-$H_2O$ should be studied.

(3) *Marine evaporates; potash deposits of the Carlsbad, New Mexico, area.* The system including all of the components of these deposits would be too complex for experimental attack. However, continuation, simplification, and extension of the classical work of Van't Hoff should help a great deal in the study of these deposits.

(4) *Problems of dolomitization.* Studies of the system CaO-MgO-$CO_2$-$H_2O$ would help a great deal in interpretations of the origin of dolomite.

### *Studies of Geologic Sampling*

Inadequate sampling, poor choosing of samples, and similar failings of the field man may render useless the most painstaking work of the chemist or spectrographer. It is by no means always evident no matter how well trained a man may

be, just what constitutes adequate sampling of a geologic unit for analytical purposes, or just where samples should be collected in order to have maximum significance.

For these reasons the Geochemistry and Petrology Branch is seeking an adequately trained statistician with the proper attitude and interests to attack the problems of geologic sampling vigorously and effectively in co-operation with geologists, chemists, and spectrographers. It is almost certain that such an individual could save the Survey the amount of his salary many times over in increased efficiency of laboratory operation; elimination of unnecessary analyses where areas have been oversampled, etc.

## 6. Conclusion

The Geochemistry and Petrology Branch of the U.S. Geological Survey has as its principal objective furtherance of as broad a programme in geochemistry and related earth sciences as is possible under existing conditions of work load and availability of funds and appropriately trained personnel.

The principal projects and activities of the geochemical part of this programme are outlined above. There are a comparable number of other projects in mineralogy, petrology, x-ray work, nucleonics, etc., that are not primarily geochemistry and are therefore not mentioned.

It is manifestly impossible to have a perfectly balanced programme in an organization of this kind, or to have one where everyone would agree as to the proper relative emphasis that should be placed on each project or research problem.

The Branch will be highly pleased, therefore, should anyone have the interest, and time, to suggest where emphasis might be shifted to advantage, to mention new projects and problems that might be pursued more profitably than some that are now under way, or to propose co-operative undertakings that could best be operated by two or more groups with different viewpoints, equipment and personnel.

It is hoped that other groups will publish summaries of geochemical work under way and definitely planned for the near future. Such summaries should be most useful in promoting co-operation, preventing duplication of effort, and speeding up research by making information more readily available by correspondence in advance of publication.

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# Determination of the isotopic ratios of silicon in rocks*

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ABSTRACT

Mass spectrometer measurements of silicon from silicate rocks indicate a maximum variation in the $Si^{28}/Si^{30}$ ratio of 1·3%. The light isotope, $Si^{28}$, shows a preference for the basic rocks, while the heavy isotope tends to concentrate in acidic and sedimentary silicates. Precious opal and sinter contain an unusually high percentage of the $Si^{28}$ isotope. These variations are believed to be the results of isotopic exchange reactions which have occurred during the geochemical and geological history of the rock.

## Introduction

For twenty years after Soddy's (1910) discovery of isotopes, an overwhelming amount of evidence was built up indicating that isotopes are identical in their chemical and physical properties, except for those properties directly related to mass, such as density of gases and condensed phases, and rates of diffusion and evaporation. It was further believed that their abundances were constant in nature, isotopes of radioactive origin being an exception in this connection.

However, in the early 1930's experimental work by Emeléus and his co-workers (1934) and theoretical work by Urey and Rittenberg (1933) indicated that variations in nature of the relative abundances of the lighter elements existed. due, for the most part, to differences in chemical properties of the isotopes. At the present time measurable abundance variations have been found in the natural, non-radiogenic isotopes of hydrogen (Report of the Committee on Measurement of Geologic Time, 1950–51; Dole, 1936a; Filippova, 1935); boron (Thode *et al.*, 1948); carbon (Nier *et al.*, 1939; Murphey *et al.*, 1941; Urey, 1948; West, 1945; McKellar, 1949); oxygen (Manian, 1934; Dole, 1936b; Thode, 1949; Urey, 1947; Epstein, 1951; Urey *et al.*, 1951; Silverman, 1951); sulphur (Thode, 1949; Macnamara *et al.*, 1950; Macnamara *et al.*, 1952); and germanium (Graham, 1951).

This investigation of silicon was undertaken with the hope of emphasizing the geological value of the information available from investigations of this nature. The usefulness of these studies to geology has already been proven in the above mentioned cases of carbon, oxygen, and sulphur; but, to the author's knowledge, no studies have been published on natural silicon variations. Any positive results for this element would have a wide application due to the fact that approximately 27% by weight of the earth's crust is silicon. Moreover, it was hoped that positive

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results would be found, due not only to the low atomic weight of the element, but also to the two mass unit separation between $Si^{28}$ and $Si^{30}$. Unfortunately, difficulties in the chemical preparation and lack of time limited the number of results to the extent that the present work can be considered only in the nature of a preliminary survey.

## Experimental

### *Sample preparation*

The silicon was introduced into the mass spectrometer in the form of silicon tetrafluoride prepared by treating the rock with hydrogen fluoride, resulting in the reaction:

$$4HF + SiO_2 \rightleftarrows SiF_4 + 2H_2O$$

The decision to use $SiF_4$ was due to the desirability of using gaseous samples

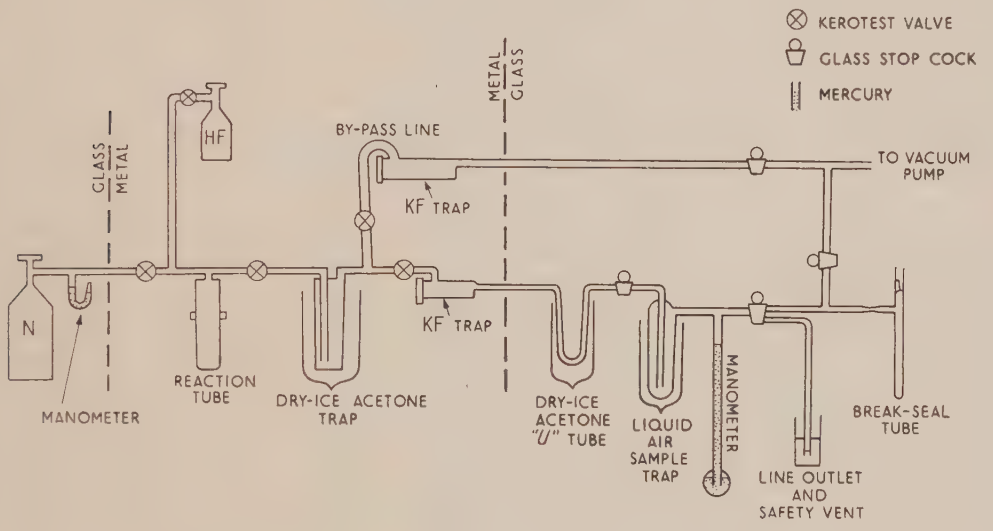


Fig. 1.

in the spectrometer, and to the fact that fluorine has only one isotope. However, the difficulties encountered by using fluorine compounds in a spectrometer may well overbalance these advantages. It is unfortunate that the gaseous compounds of silicon are limited in number and are quite active.

Several precautions were necessary in the preparation of $SiF_4$. No siliceous material other than the rock sample could come in contact with the HF. It was necessary to remove quickly and completely the water formed during the reaction, not only to prevent possible fractionation of the silicon as the reaction reversed, but also to avoid HF being formed in areas where glass was present.

The sample preparation line, shown in Fig. 1, was kept under vacuum except during a run, at which time it was flooded with a pure dry nitrogen at atmospheric pressure. That part of the line in contact with the HF was constructed of copper,

or when low heat conductivity was desired, stainless steel. Details of the metal components are shown in Fig. 2. "O" rings set in flanges were used where it was necessary to open the line. The metal components were joined by quarter-inch copper tubing and flared joints. The Kerotest valves were nickel-plated and provided with neoprene washers and packing. The glass to metal seals were made by silver soldering a sleeve over the copper tubing, inserting a quarter-inch glass tubing into this sleeve, and sealing the glass-sleeve junction with sealing-wax.

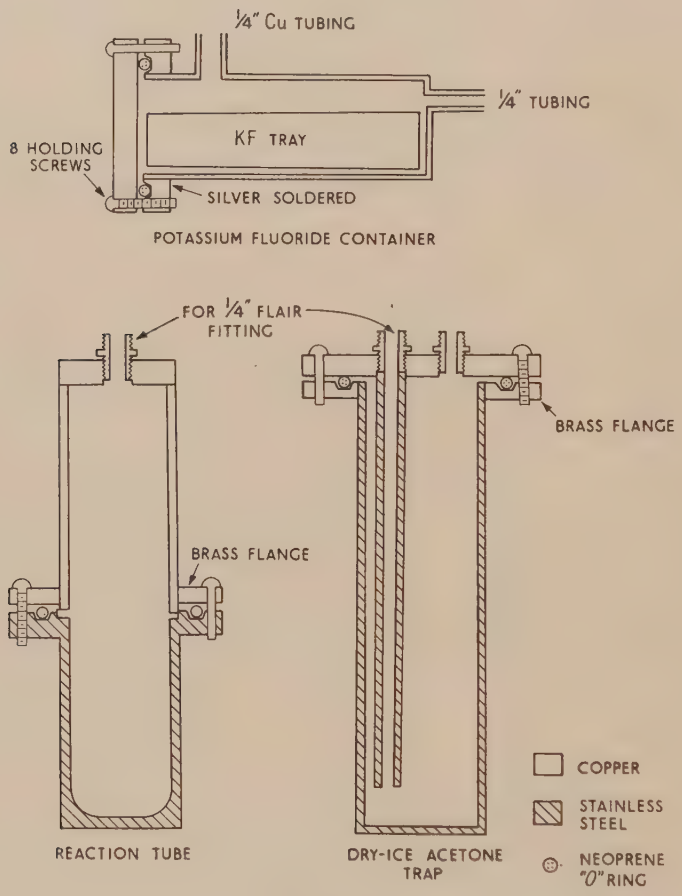


Fig. 2.

The glass stopcocks were lubricated by Apiezon Grease "N". Tests showed that no volatile compounds were formed by HF reacting with the line materials.

The rock to be analyzed was crushed to 100 mesh, boiled in nitric acid, boiled in hydrochloric acid, washed, and boiled in water. It was then heated to drive off any occluded gases.

In preparing for a run the line was carefully cleaned and the potassium fluoride changed. The line was heated with the rock sample in the reaction tube, and then

evacuated for at least eight hours to insure the removal of gases and water vapour. The reaction tube was then isolated and immersed in liquid air, the HF tank was opened, and a small quantity of HF vapour was condensed on the crushed sample rock. The entire line, with the exception of the by-pass line and the vacuum line, was then flooded with nitrogen which was adjusted for a small positive flow by way of the outlet.

The removal of the liquid air from around the reaction tube started the chemical process. The dry-ice acetone trap removed the water vapour and a large percentage of the free HF, while the KF removed the remaining HF. The dry-ice, acetone "U" tube was a further precaution against water vapour. The $SiF_4$ solidified in the liquid-air sample trap. Finally the reaction tube was heated in boiling water to decompose any fluosilicic acid ($H_2SiF_6$) formed. After the evacuation of the line to insure complete collection of the $SiF_4$, the sample trap and break seal tube were isolated. The liquid air was transferred to the break seal tube, dry ice and acetone were substituted around the sample trap, and the $SiF_4$ was distilled into the break seal tube to be stored until analysis on the spectrometer.

To insure that no fractionation was occurring during the chemical preparation, a series of runs was taken on several samples using various amounts of HF, varying preparation times, and collecting several $SiF_4$ samples from the same rock without opening the line. Rocks were also rerun several weeks apart. In no instance were abundance variations detected.

### *Mass spectrometry*

The mass spectrometer employed was a 180° direction-focusing Nier type with a resolution of one mass unit in 300. It was normally used with automatic magnetic scanning, the ion current intensity being recorded by a *Speedomax Pen Recorder*. A complete description of this instrument has been given by C. B. Collins (1951).

On preliminary analyses it was found that automatic magnetic scanning did not give the required accuracy. To correct for this the magnet current was kept steady and the accelerating voltage was manually varied over the required mass range. As absolute results were not desired, increased accuracy was gained by the use of a standard sample with which all others were compared. This not only corrected for long term linear changes in the shunt resistors and mass spectrometer components, but also nullified absolute errors such as fractionation in the capillary leak feeding the sample into the spectrometer tube, nonlinearity of the shunt resistors, and like factors.

The actual isotopic analysis was made on the peaks of the $SiF_3$ ions of masses 85, 86 and 87. Not only did these ions give the maximum signal intensity, but they are also without mass contaminations to which the other ions are subject in the form of boron trifluoride and sulphur dioxide in the $SiF_2$ mass range of 66, 67 and 68; carbon dioxide in the SiF range of masses 47, 48 and 49; and nitrogen in the Si mass range of 28, 29 and 30.

A search of the mass spectrum revealed only one contaminating gas in any quantity. This gas, which composed $\frac{1}{2}$ to 2% of every sample appeared as masses 82, 83 and 84, and was believed, from its abundance ratio, to be $SiOF_2$. It is not

known whether this gas was a stable compound or an ion formed within the spectrometer tube. No contamination of the 85 through 87 mass range was found.

## Results

The silicon isotopic abundances obtained for various rocks are listed in Table 1 in order of increasing $Si^{28}/Si^{30}$ ratio. All results are relative to the standard, high temperature quartz from Madoc, Ontario, which had the value 29·75. It is interesting to note that these results are in close relative agreement with the results obtained by Silverman (1951) for the variation of the oxygen isotopes in silicate rocks.

*Table* 1. *Abundance of the silicon isotopes in silicate rocks**

| *Number* | *Description of Sample* | *Ratio* $Si^{28}/Si^{30}$ | *Date prepared* | *Date analyzed* |
|---|---|---|---|---|
| 37–6 | Low temperature quartz, Keokuk, Iowa | 29·68 ± 0·02 | 8 April 1952 | 18 June |
| 56–15 | Tripolite, California | 29·73 ± 0·02 | 16 May 1952 | 22 May |
| 57–10 | Radiolaria Earth, Barbadoes | 29·73 ± 0·05 | 23 May 1952 | 30 May |
| Standard | High temperature quartz, Madoc, Ontario | 29·75 | 28 March 1952 | |
| 39–19 | High temperature quartz, Lamaque Mine, Quebec | 29·77 ± 0·02 | 11 April 1952 | 8 May |
| 40–16 | High temperature quartz, Renfrew County, Ontario | 29·79 ± 0·03 | 12 April 1952 | 30 April |
| 36–17 | High temperature quartz, Hybla, Ontario | 29·86 ± 0·03 | 7 April 1952 | 30 April |
| 59–47 | Basalt with olivine enclosures, Paia Maui, Hawaii | 29·86 ± 0·02 | 26 May 1952 | 18 June |
| 44–44 | Dolerite, Shikapur, India | 29·96 ± 0·03 | 21 April 1952 | 10 May |
| 43–43 | Basalt, Maui, Hawaii | 30·02 ± 0·04 | 19 April 1952 | 29 May |
| 54–8 | Precious opal, southern Australia | 30·09 ± 0·04 | 9 May 1952 | 20 June |
| 53–13 | Sinter, Yellowstone | 30·10 ± 0·04 | 6 May 1952 | 16 June |

* Sources and descriptions of these samples are listed in the appendix.

These silicon variations, while smaller than those found for oxygen, carbon, and sulphur, are of the order expected from geochemical considerations. The largest separation effects occur in gaseous exchanges, but the only silicon gas found to any extent in nature is $SiF_4$, which is found only in small localized areas. Furthermore, silicon, silica and most silicates are extremely insoluble in water, thus reducing the possibilities of large scale low-temperature exchanges of the solid-liquid type.

In attempting to explain the variations found, the author was greatly aided by a theoretical study by F. S. Grant (1951) on the causes of fractionation among

the silicon isotopes. GRANT pointed out that in order to calculate, by use of statistical mechanics, the isotopic fractionation of the silicate, it is necessary to assume that the probability of the silicon exchange is governed by the external vibrations of the $SiO_4$ ion alone, and that these vibrations are not affected by polymerization, an assumption that is very probably accurate for unpolymerized orthosilicates such as topaz and zircon. However, recent work on the infrared reflection spectra of silicate crystals (SCHAEFER *et al.*, 1934; MATOSSI *et al.*, 1936) suggests that, in general, the fundamental frequencies of the $SiO_4$ ion are increased with increased polymerization. This effect does not appear to be very large, but it was observed that for crystals with high polymerization the spectral bands were blurred and diffuse, suggesting "blurring" of the individual modes. Furthermore, it can be shown that the lattices vibrating with the higher frequencies prefer the heavier isotope. In general the simpler silicate structures are in the basic rocks, while the complexity and hence the polymerization of the lattices increases as the rocks become higher in silica. Therefore, it may be postulated that the heavy isotope should concentrate in the silica-rich rocks.

On the other hand, present geologic thought is that igneous rocks are derived by differentiation from a magma, the basic rocks being the first to crystallize and the high-silica types such as granite the last (see, for example, SHAND, 1947). If this theory is correct, we should expect, on the basis of energy considerations, that the earlier crystallizing rocks (i.e. the basic ones) would be highest in the heavy isotope. As these experimental results show the heavy isotopes to prefer the silicic rocks, it may be that either the increased vibrational frequency of the lattices is the dominant separation effect or that the theory of magmatic differentiation is not completely correct.

The result obtained for the low temperature quartz from Keokuk indicates that the deposition of silica from mineralizing solutions is accompanied in the precipitated stage by heavy isotope enrichment. The temperature of formation of this quartz is 100°C to 200°C as compared to above 570°C for high temperature quartz. As the equilibrium constant between silica and the mineralizing solution should have a higher value for the low temperature specimen, the equilibrium constant must favour $Si^{30}$ in the quartz. Added proof of this is furnished by SILVERMAN, who found that the $O^{18}/O^{16}$ ratio for a rock varied directly with the amount of secondary silica in that rock.

Sample No. 56-15, known as tripole, tripolite, or diatomaceous earth, is from extensive California beds that were formed from organisms such as radiolarians, diatoms, and sponges which form tests of hydrated, opaline silica. The diatom skeletons predominate in the California beds. The close agreement between tripolite and radiolarian earth from Barbadoes indicates that diatoms and radiolaria have skeletons of similar isotopic composition.

Precious opal and sinter, both of which are secondary siliceous deposits, appear to have an unusually high $Si^{28}$ content. Sinter is deposited around hot springs when silica in solution is precipitated due to evaporation, mixture with other hot waters, or the action of hot water algae (LINDGREN, 1933); opal is believed to be an amorphous, transparent, hard gel of silica containing water and is transported in the colloidal state by aqueous solutions (SOSMAN, 1927). The

preference of these two rocks for the lighter isotope cannot be attributed to a chemical effect because precious opal, sinter, and tripolite, which is low in $Si^{28}$, are chemically the same. Likewise, it does not appear that any biochemical effect is responsible, for, in those cases where bacteria are active, they reduce the colloidal suspension of the silica, but do not otherwise enter into the process. It also appears unlikely that the method of deposition can cause this fractionation, as flint, which is also formed from silica colloidally suspended in shallow waters, was found by Silverman (1951) to have an oxygen isotopic abundance similar to diatomite. Therefore, it appears that the opal and sinter must have been deposited from a solution enriched in $Si^{28}$. The mineralizing solutions for these rocks consist almost entirely of circulating ground water containing silica from subsurface leaching. In a liquid-solid system the light isotope tends to concentrate in the liquid phase. Therefore, this ground water should have a high $Si^{28}$ content. This effect would be increased by the low temperatures of this reaction, and the continued reworking of the materials. Some idea of the fractionation obtained can be realized from the fact that the Yellowstone sinter is deposited from water circulating through rhyolite, which should have an isotopic composition similar to quartz.

## Conclusion

It should be emphasized that, due to the small number of samples analyzed, the results of this paper are in no way conclusive. However, it does appear that abundance measurements of silicon do reflect the geologic and chemical histories of the silicate rocks.

The author would like to express his sincere thanks to Professor J. T. Wilson under whose direction this work was done and whose help and encouragement were determining factors in its successful completion. He would also like to thank Dr. C. B. Collins for his valuable aid in the mass spectrometry of the problem, Dr. F. G. Smith for his help and advice on the silicon samples, and Dr. F. S. Grant for making available his theoretical work on the equilibrium constants and structures of the silicates. Thanks are also due to Mr. R. M. Farquhar and Mr. R. D. Russell for their aid in obtaining satisfactory results with the mass spectrometer.

## Addendum

While this manuscript was being prepared a comprehensive review of non-radiogenic isotopes was published by Ingerson (1953). Reference is made in this article to a paper by Reynolds and Verhoogen (1953) on the variations in the isotopic constitution of silicon from minerals and rocks. Their results seem to be in relative agreement with those listed here, but the total variation found was only 0·3%. The author has not seen this paper and is unable to explain this discrepancy.

## Appendix

### Description of Rock Samples

| *Number* | *Description* | *Donor* |
|---|---|---|
| 37–6 | Low temperature quartz from Keokuk, Iowa. Small crystals from geode formed less than one mile below surface | Dr. F. G. Smith |
| 56–15 | Opal-variety tripolite, from Santa Barbara County, Calif. Royal Ontario Museum #M11174 | Dr. V. B. Meen |
| 57–10 | Radiolaria Earth, Bissex, Barbadoes. Royal Ontario Museum #10880 | Dr. V. B. Meen |
| Standard | High temperature quartz, Ackerman Mine, Madoc, Ontario | |
| 39–19 | High temperature quartz, from hangwall of 80–13 vein on 825 foot level, Lamaque Mine, Abitibi County, Quebec | Dr. F. G. Smith |
| 40–16 | High temperature quartz, from pegmatite, Lat. 23, Concession 15, Renfrew County, Ontario. A. D. Graham Collection | Dr. F. G. Smith |
| 36–17 | High temperature quartz, from pegmatite, McDonald Quarry, Hybla, Ontario | Dr. F. G. Smith |
| 59–47 | Basalt with olivine enclosures, from Paia Maui, Hawaii. Geology Department #PO-08 | Dr. W. W. Moorhouse |
| 44–44 | Dolerite, from #1 Lava Sheet, Shikapur, India. Geology Department #PO-451 | Dr. W. W. Moorhouse |
| 43–43 | Basalt, from Maui, Hawaii. Geology Department #PO-02 | Dr. W. W. Moorhouse |
| 54–8 | Precious Opal, from Australia. Exact source unknown | Dr. J. T. Wilson |
| 53–13 | Yellowstone sinter. Royal Ontario Museum #C-946 | Dr. V. B. Meen |

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